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Development and Optimization of Multi-Functional SCR-DPF Aftertreatment for Heavy-Duty NO_x and Soot Emission Reduction

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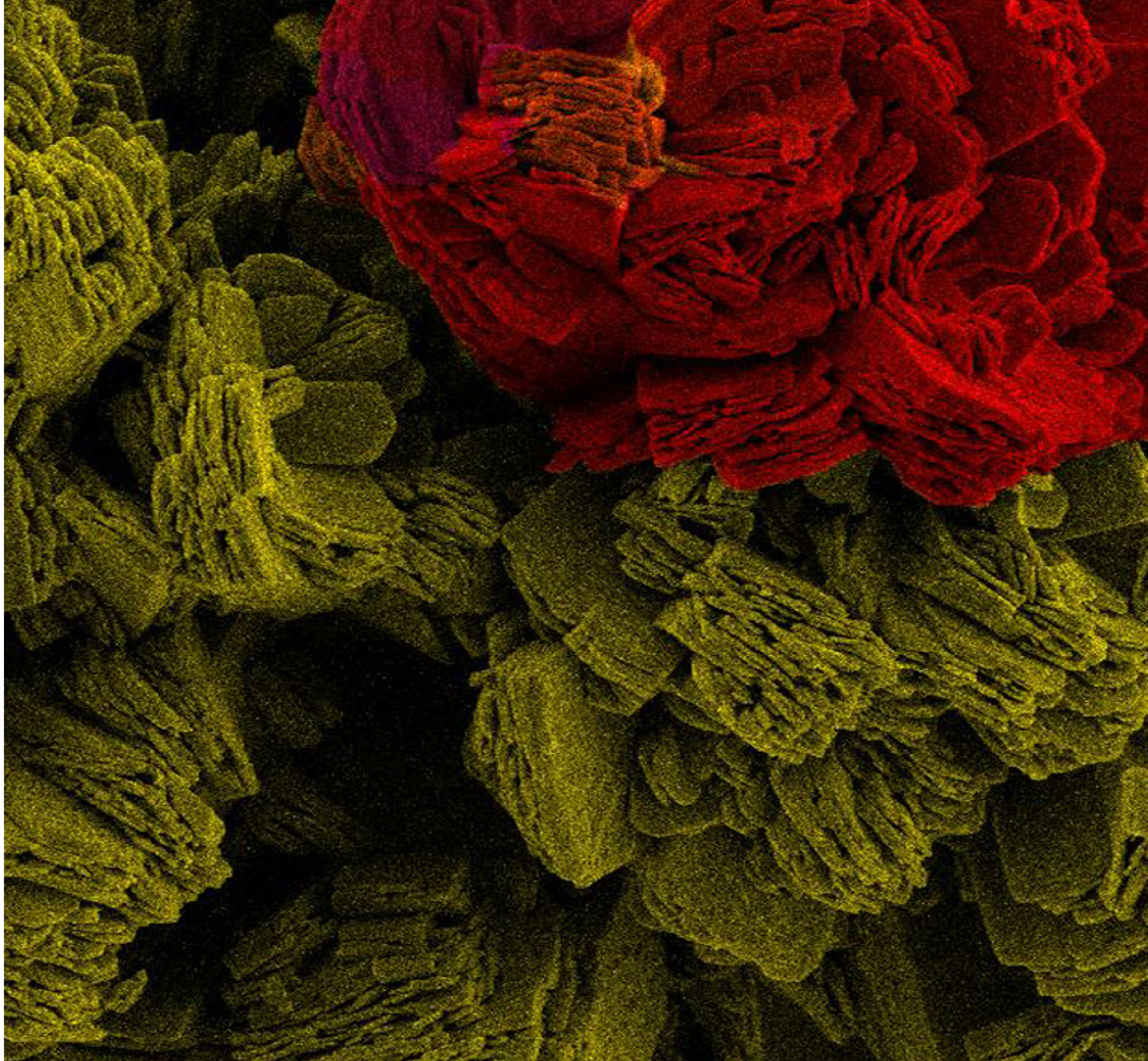

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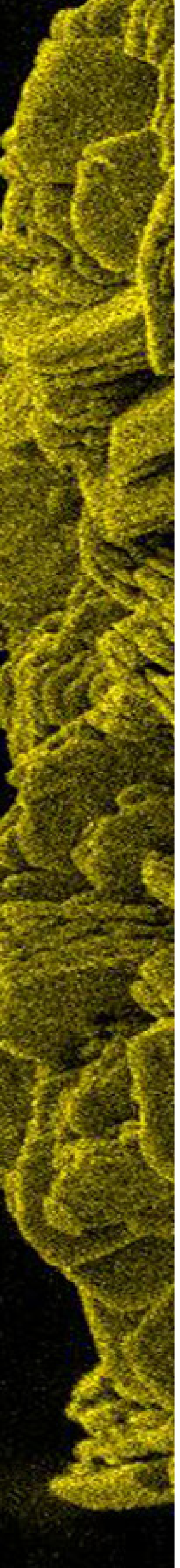
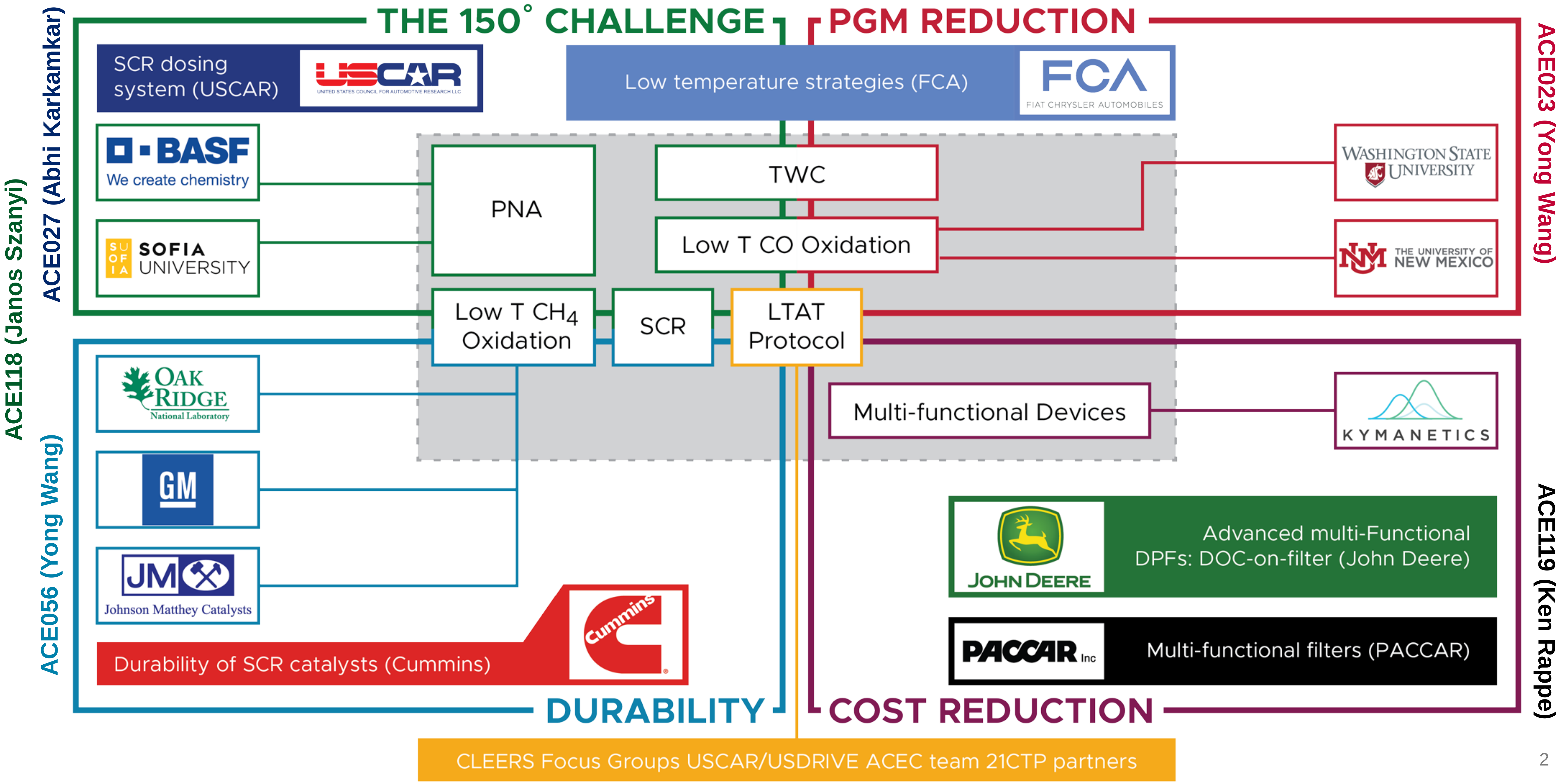
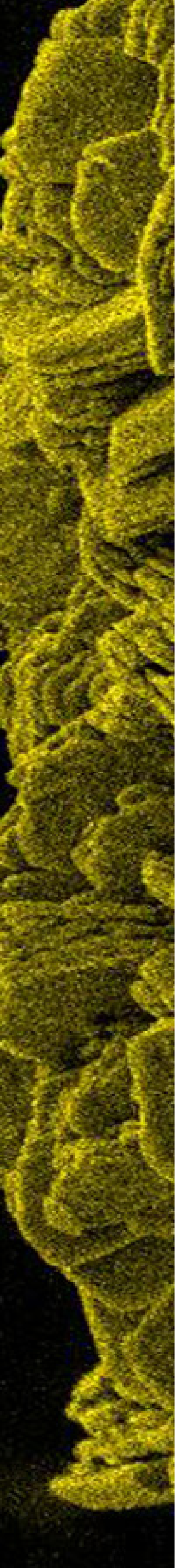


PNNL Fundamental and CRADA Projects Address the 150℃ Challenge, PGM Reduction, Durability, and Cost - Exemplified by 5 AMR Presentations





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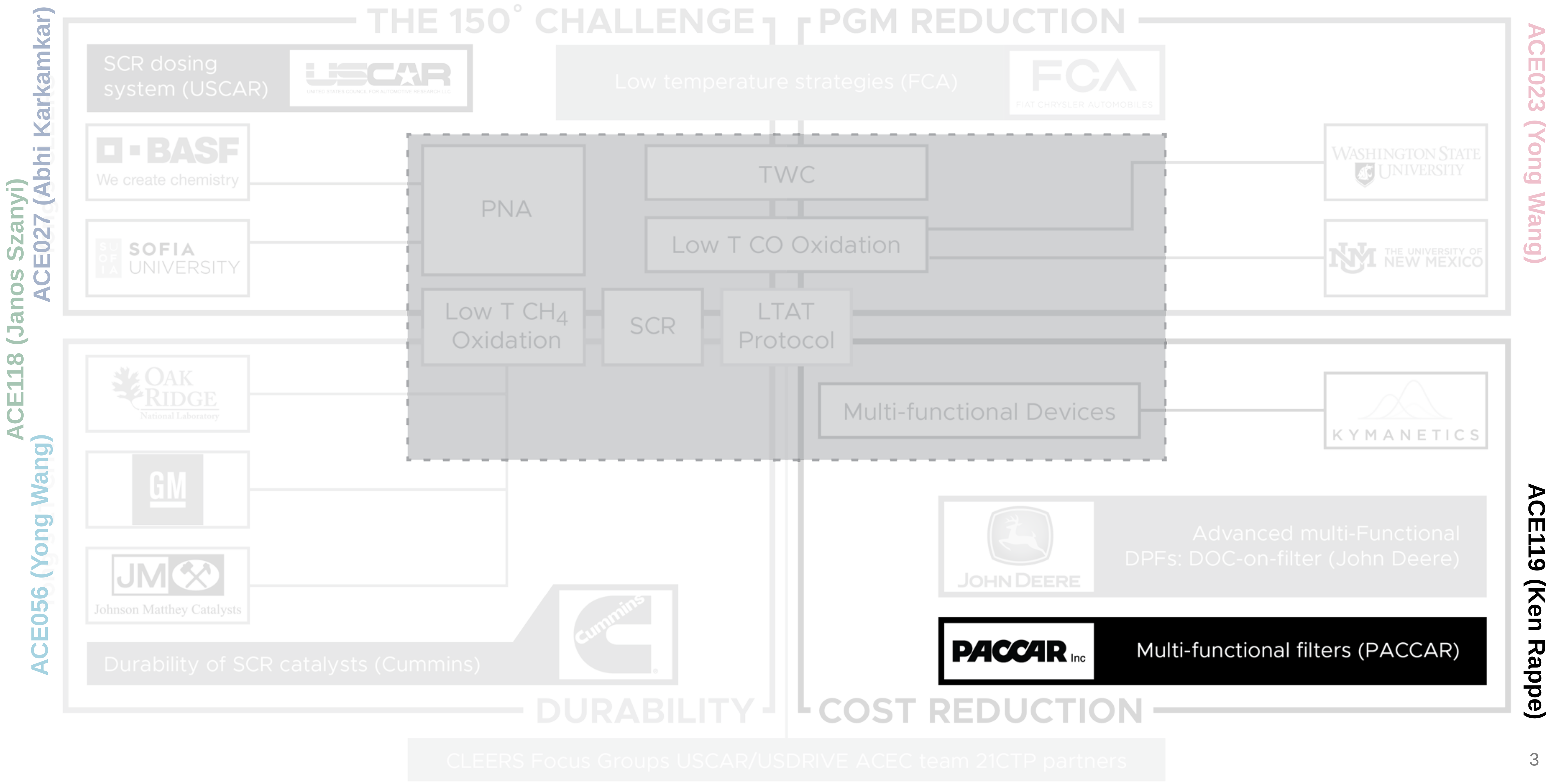


Project Overview

Timeline

- 4-yr CRADA
  - Start date – July 2016
  - End date – June 2020
- 95% complete

Barriers

- **B. Lack of cost-effective emission control** for meeting EPA standards for NOx & PM emissions
- **E. Durability** of the emission control system: 435,000 miles (HD)
- **G. Cost of emission control** devices… for heavy duty engines in particular

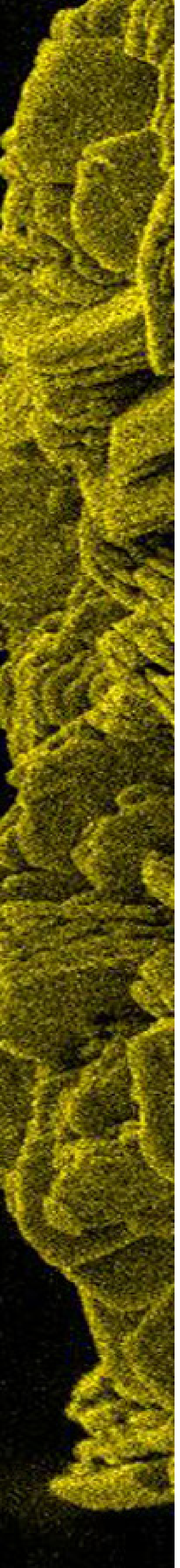
Budget

- Contract value – $2.7M
  - $1.35M DOE share
  - $1.35M PACCAR share
- Funding received
  - $1.1M through FY18
  - FY20 – $100K

Partners

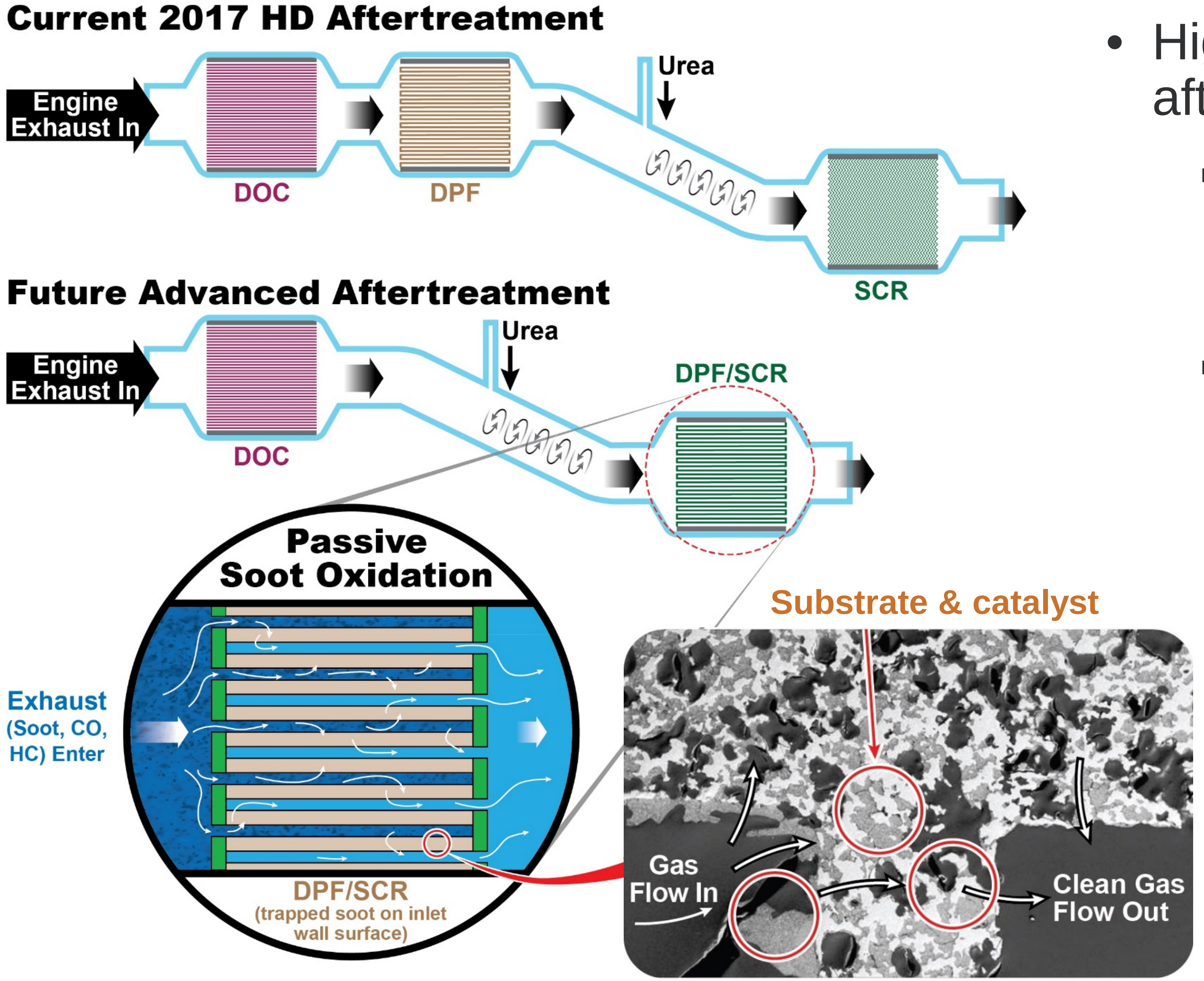
PACCAR Inc

- CRADA partner



Relevance

Multi-Functional Aftertreatment: SCR-on-DPF for HD



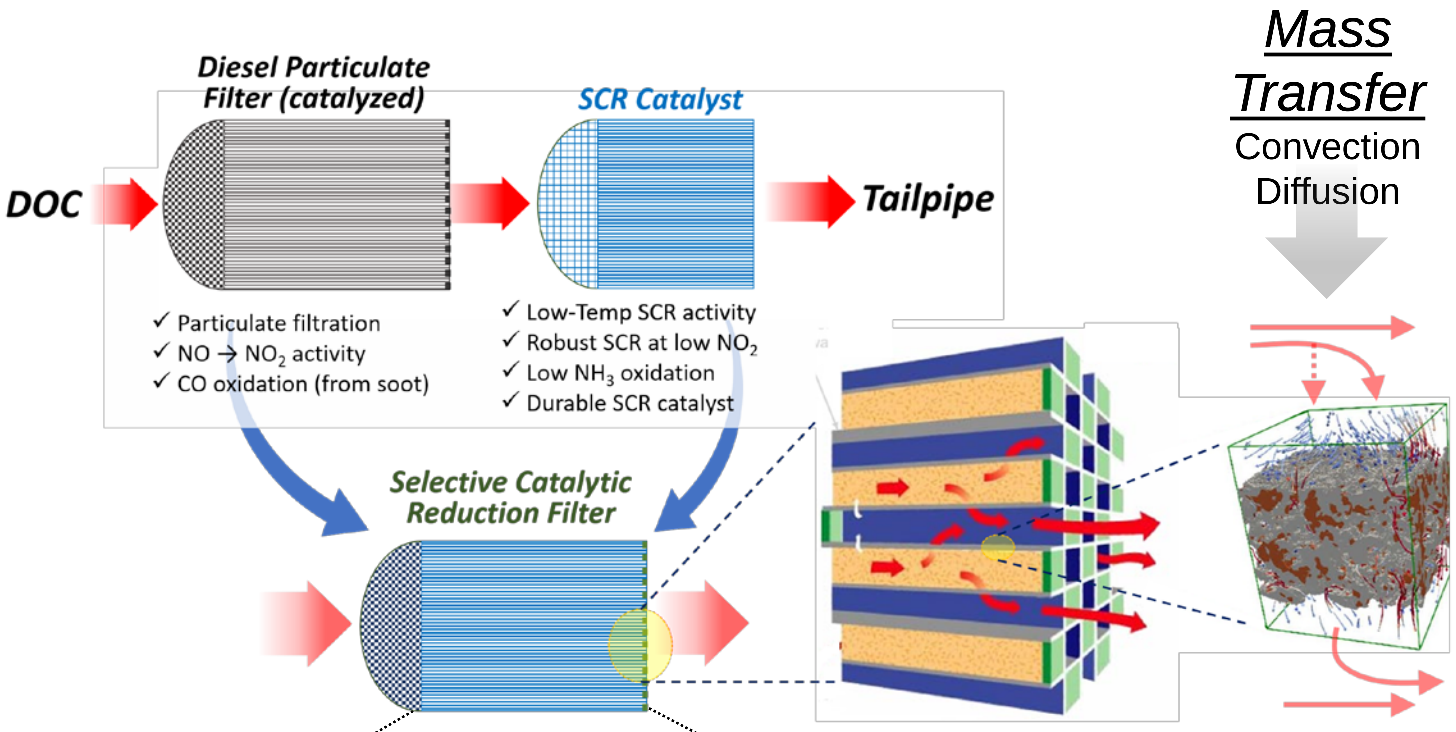
- Highly promising strategy of aftertreatment integration
  - Reduced total thermal mass
    - ✓ **Faster warm-up**
    - ✓ **Reduced cold-start emissions**
  - Improved performance & increased flexibility
    - ✓ **SCR more closely coupled to engine**
    - ✓ **Increased total SCR volume**

✓ **Soot trapped upstream**

✓ **Molecular diffusion to washcoat**

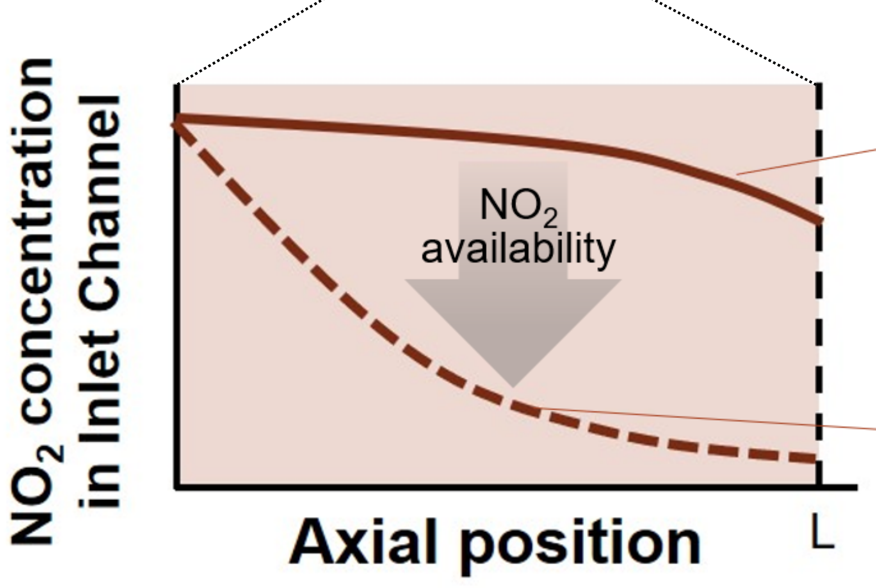
Relevance

Fast SCR depletes NO_2 in inlet channel leaving less for passive soot oxidation



Challenges to deployment

1. SCR performance (enough SCR)
2. SCR durability (extreme temps)
3. ***Passive soot oxidation***



$$C\,(soot) + 2\,NO_2 \longrightarrow CO_2 + 2NO$$ **Passive soot oxidation**

$$C\,(soot) + 2\,NO_2 \longrightarrow CO_2 + 2NO$$ **Passive soot oxidation**

+

$$2\,NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O$$ ***Fast SCR***

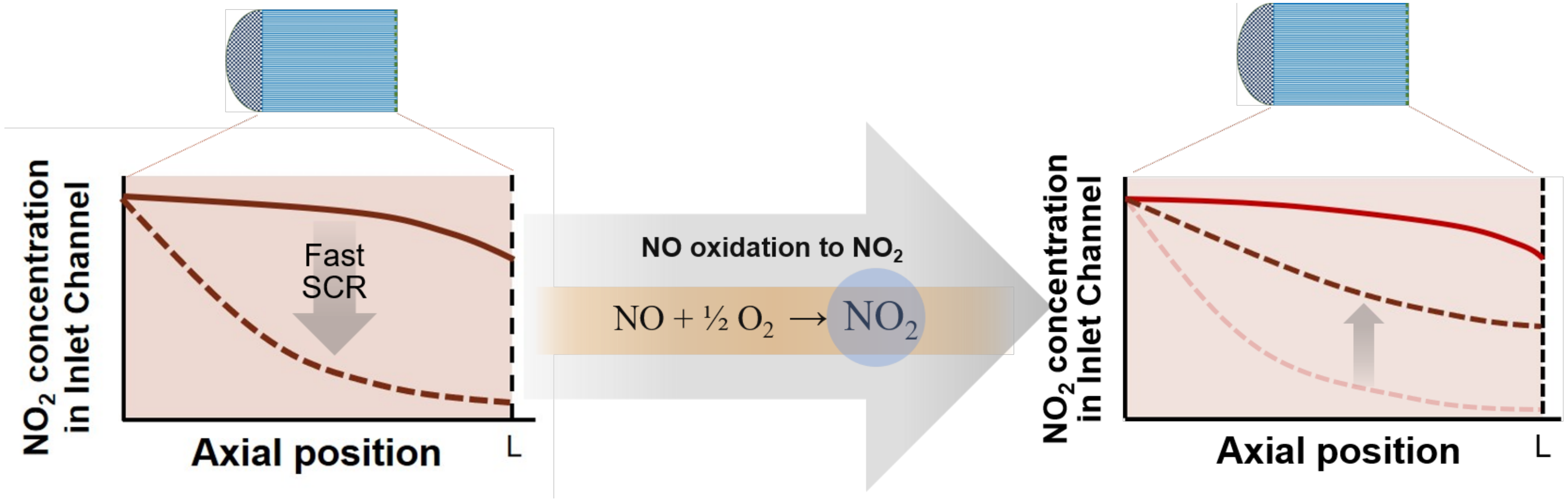
The role of the SCO phase

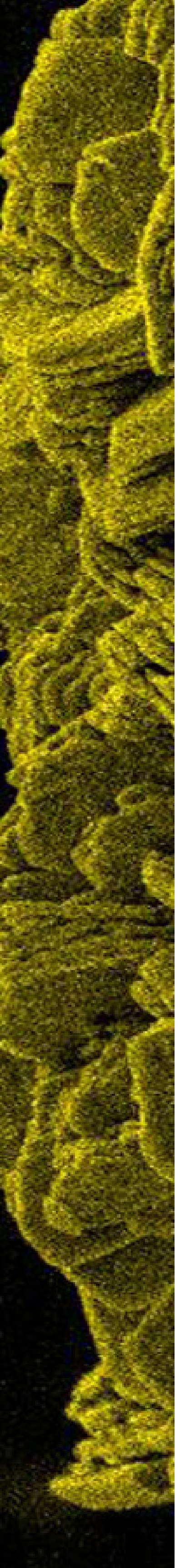
Goal: Maximize passive soot oxidation activity with SCR on filter

Approach: Minimize the impact of fast-SCR catalysis on inlet NO_2
***This is a catalysis challenge*.**

- Use a selective catalytic oxidation (SCO) phase with the SCR catalyst to promote oxidation of NO to NO_2
- Increase NO_2 in the filter inlet channel by ***reducing NO_2 forward diffusive effects***

- Mn-based SCO phase being pursued

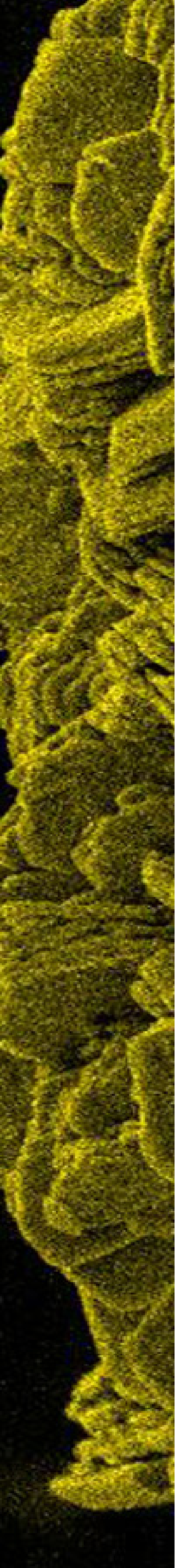




Approach

Schedule and Milestones

Date	Milestone and Go/No-Go Decisions	Status
May 2019	Milestone: SCRF single wall model complete	Complete
July 2019	Go/No-Go decision: SCO-SCR binary catalyst demonstrated that exhibits improved SCR/PSO performance and durability	Complete (PNNL + PACCAR)
Feb 2020	SMART milestone: SCRF binary catalyst development complete	Complete
April 2020	Milestone: SCRF device-level model complete	On-going



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Accomplishments

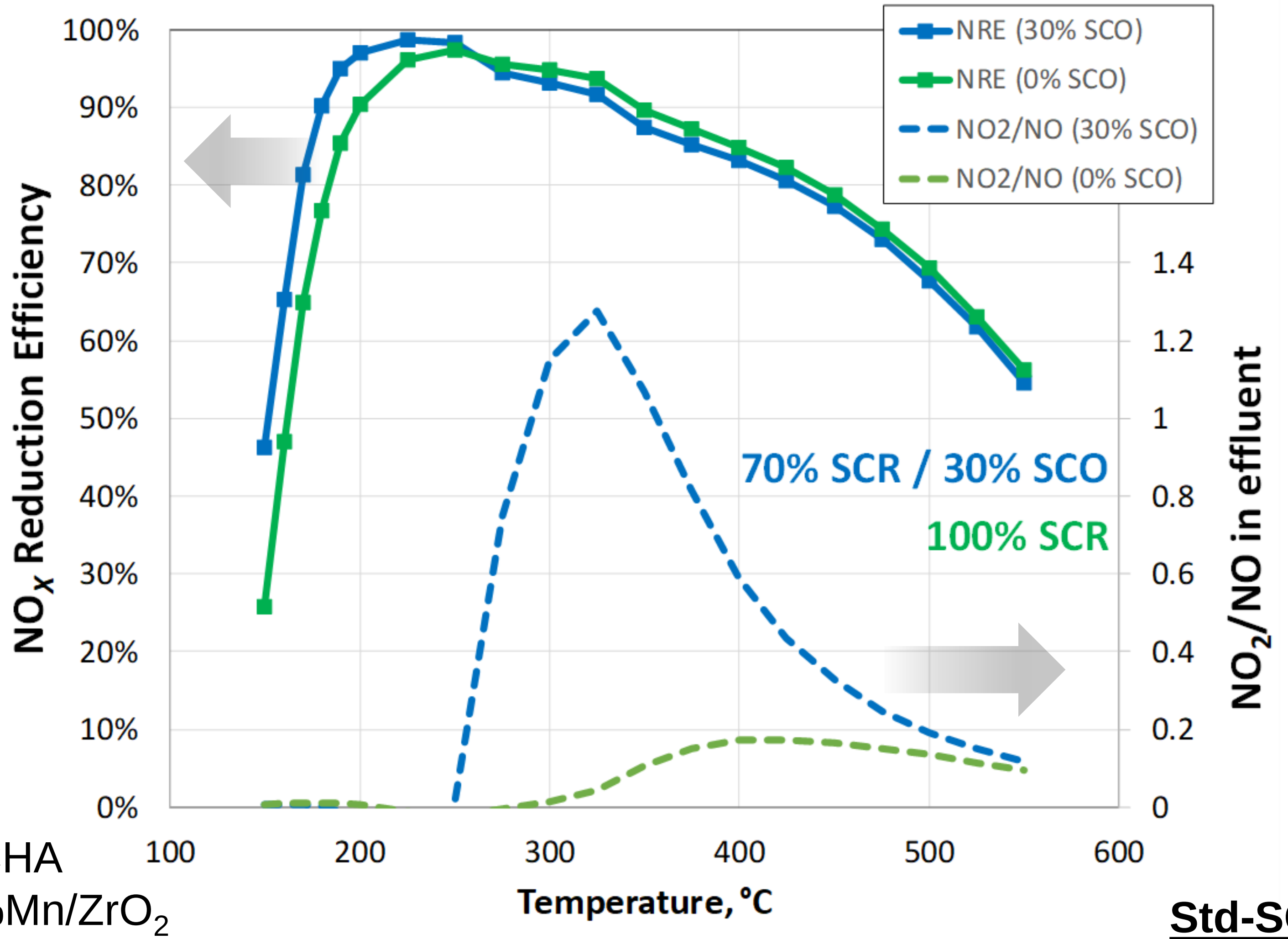
Focus for this year's efforts

- Core sampling testing
  - SCR = CuCHA
  - SCO = 10%Mn/ZrO_2
  - Most work is comparing
    - ✓ 100% SCR
    - ✓ 30% SCO – 70% SCR physically mixed (intimate)
- Axisuite modeling in progress
- SCO phase study and path forward

Accomplishments

SCO phase shown to significantly shift NO_2/NO_x balance with equivalent or superior SCR performance

- Core sample testing – ***Std SCR conditions***
- ~70 g/L active phase on SiC support

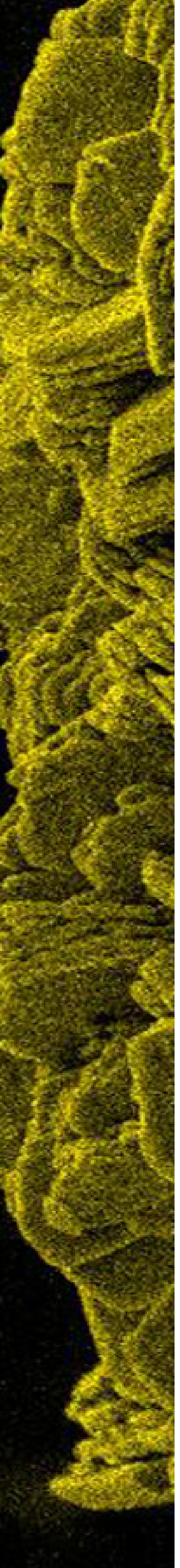


SCR = CuCHA
SCO = 10%Mn/ZrO_2

- Low temperature SCR activity improvement
- <u>*No adverse impact of NH_3 oxidation at elevated temperature*</u>
- Significantly increased NO_2 in catalyst effluent
  - 290°C to 360°C

NO_2 > NO in effluent

<u>**Std-SCR Conditions**</u>:
300 ppm NO, 10% O_2, 6% H_2O, Balance N_2, SV=35K/hr



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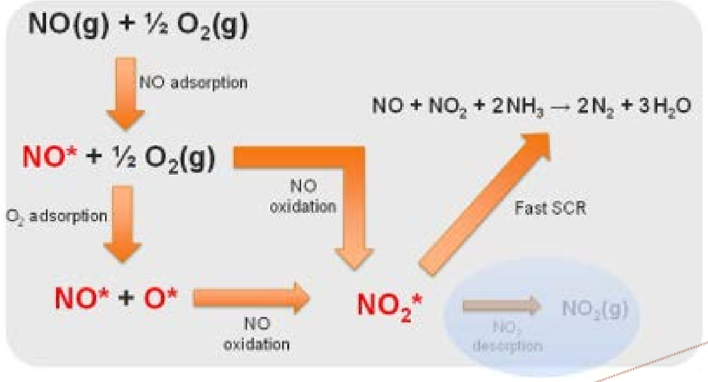
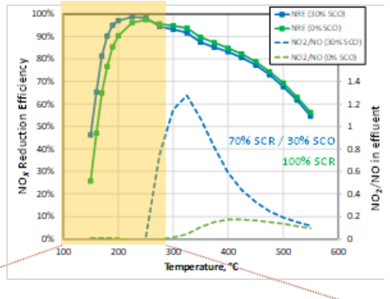
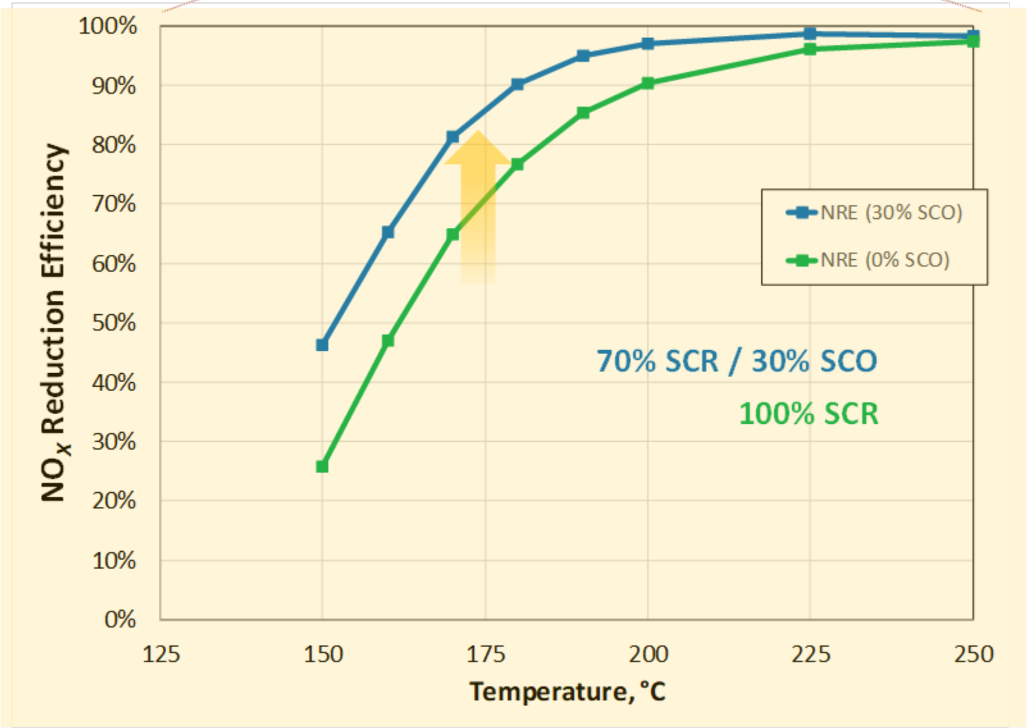
Accomplishments

SCO-SCR synergistic interaction observed from superior low-temperature SCR performance







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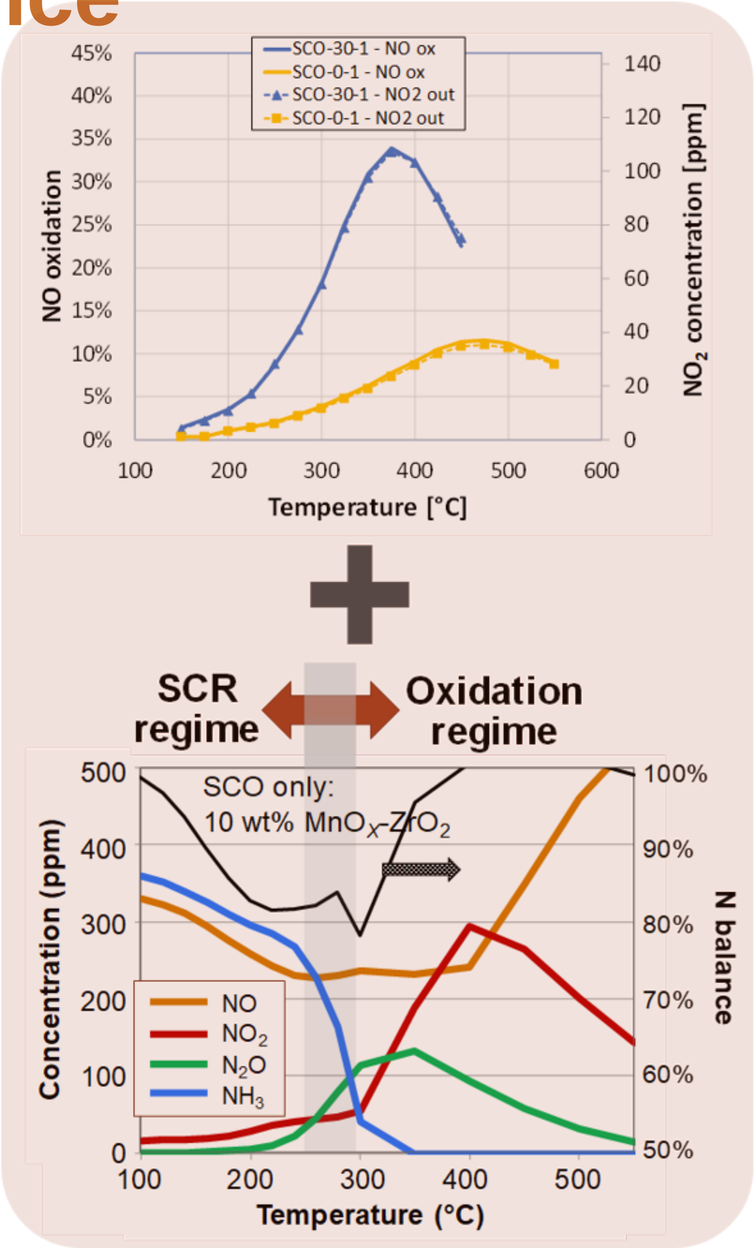
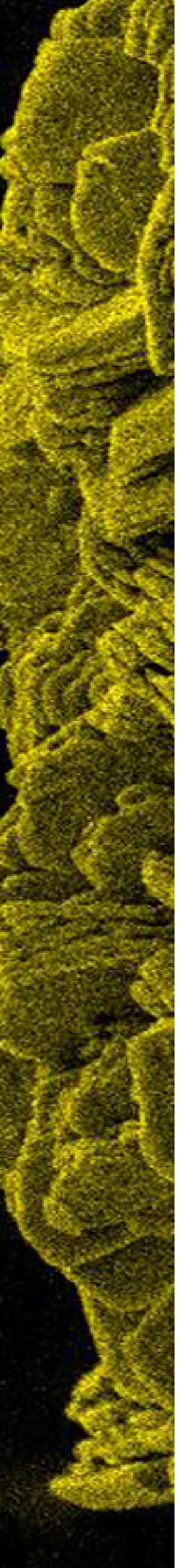
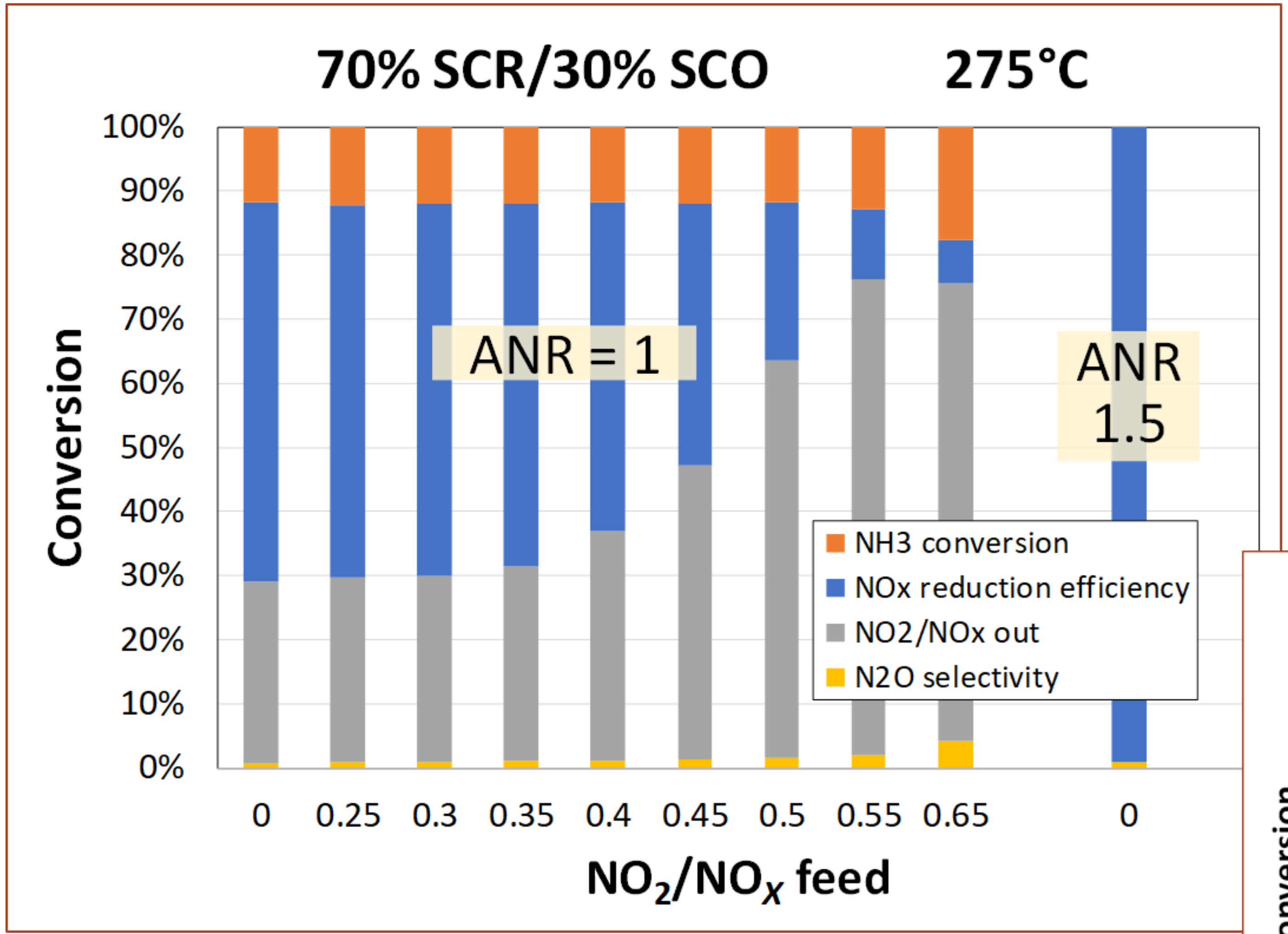


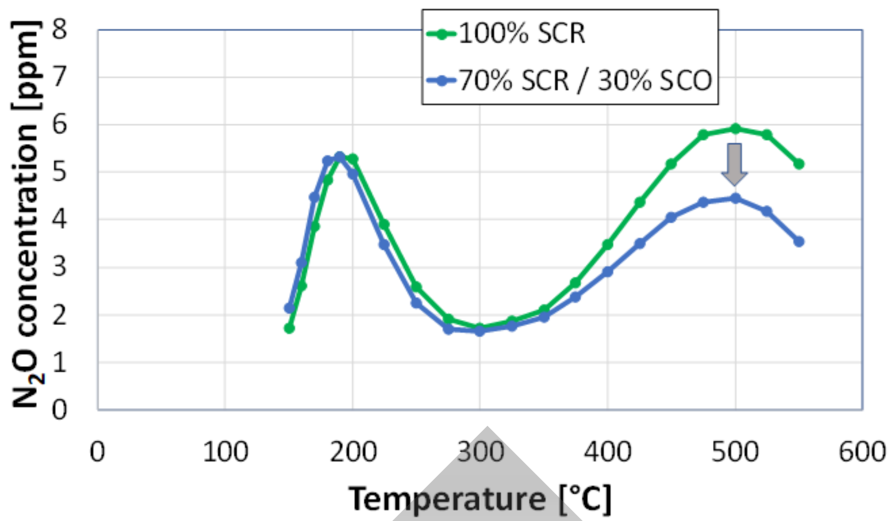
Low-temperature SCR performance improvement from binary catalyst > NO oxidation + SCO-phase SCR contribution



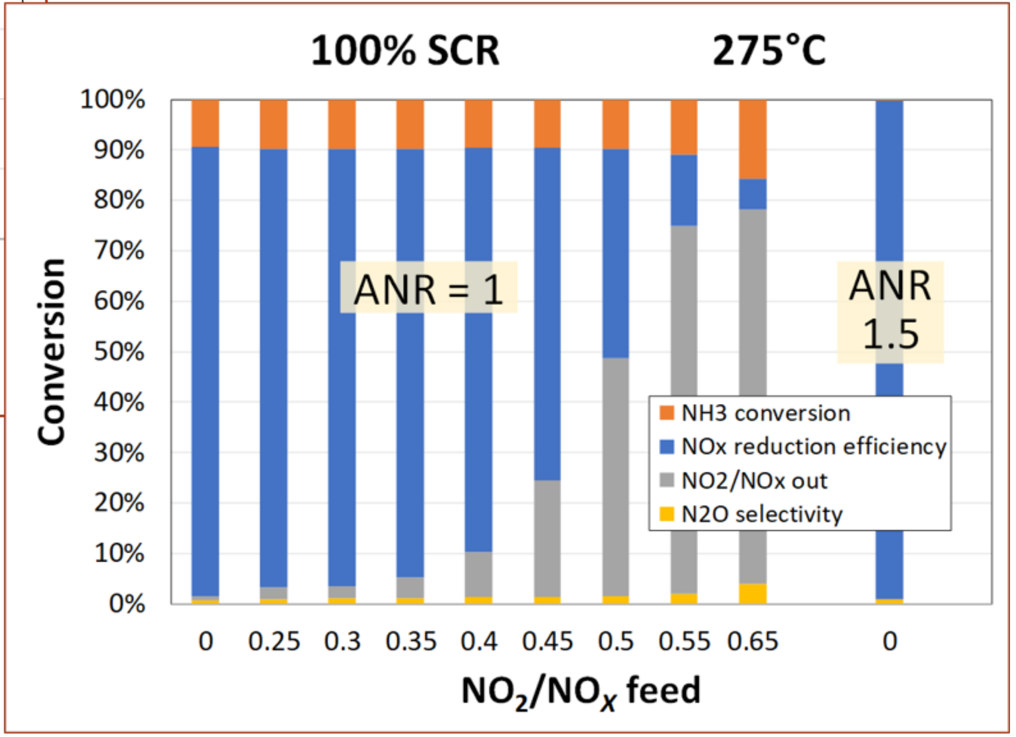
Accomplishments

SCO phase exhibits durable impact on NO_2/NO_x balance across all expected gas compositions

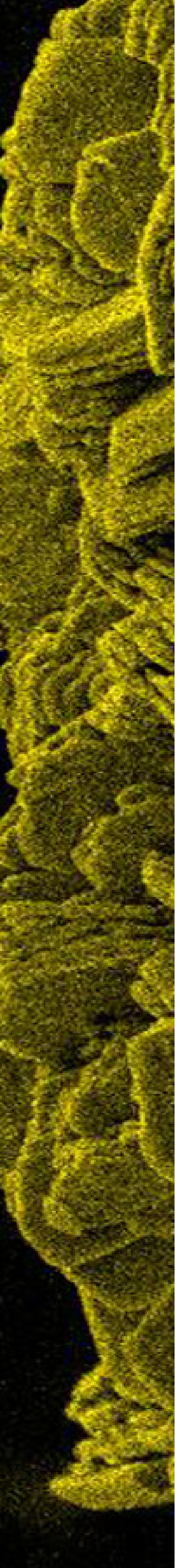




Analogous or improved N_2O effluent profile!



SCO contribution has durable impact across broad NO/NO_2 make-up



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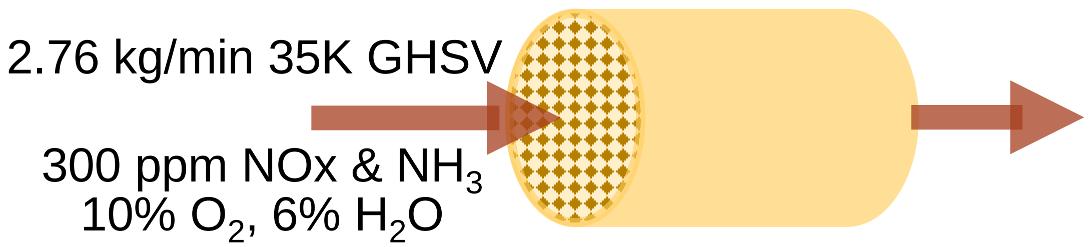
Approach

Soot oxidation testing procedure

Soot loading & soot oxidation are decoupled and performed iteratively

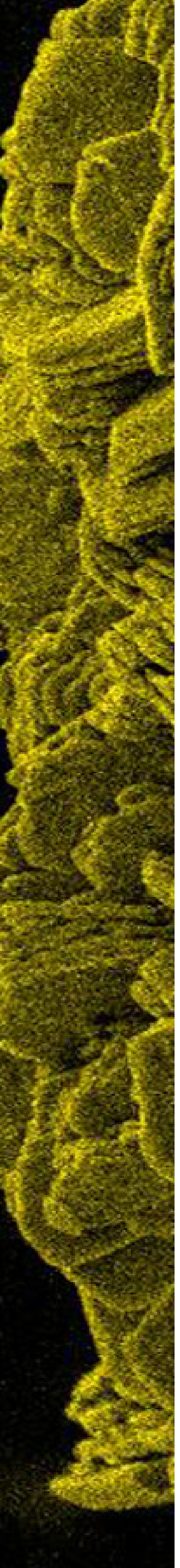


<u>Sequence</u>

- Load to ~4 g/L soot loading on real soot generator unit
- Remove from soot generator apparatus, install into synthetic gas bench
- Pre-heat and stabilize inlet gas profile
- Temperature programmed oxidation @ 5°C/min 150°C (or 180°C) to 580°C

<u>Metrics</u>

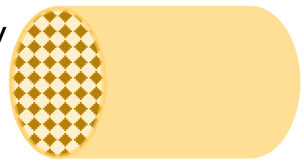
- Pressure drop
- CO, CO_2 production
  - Soot mass is not reliable on mini-cores



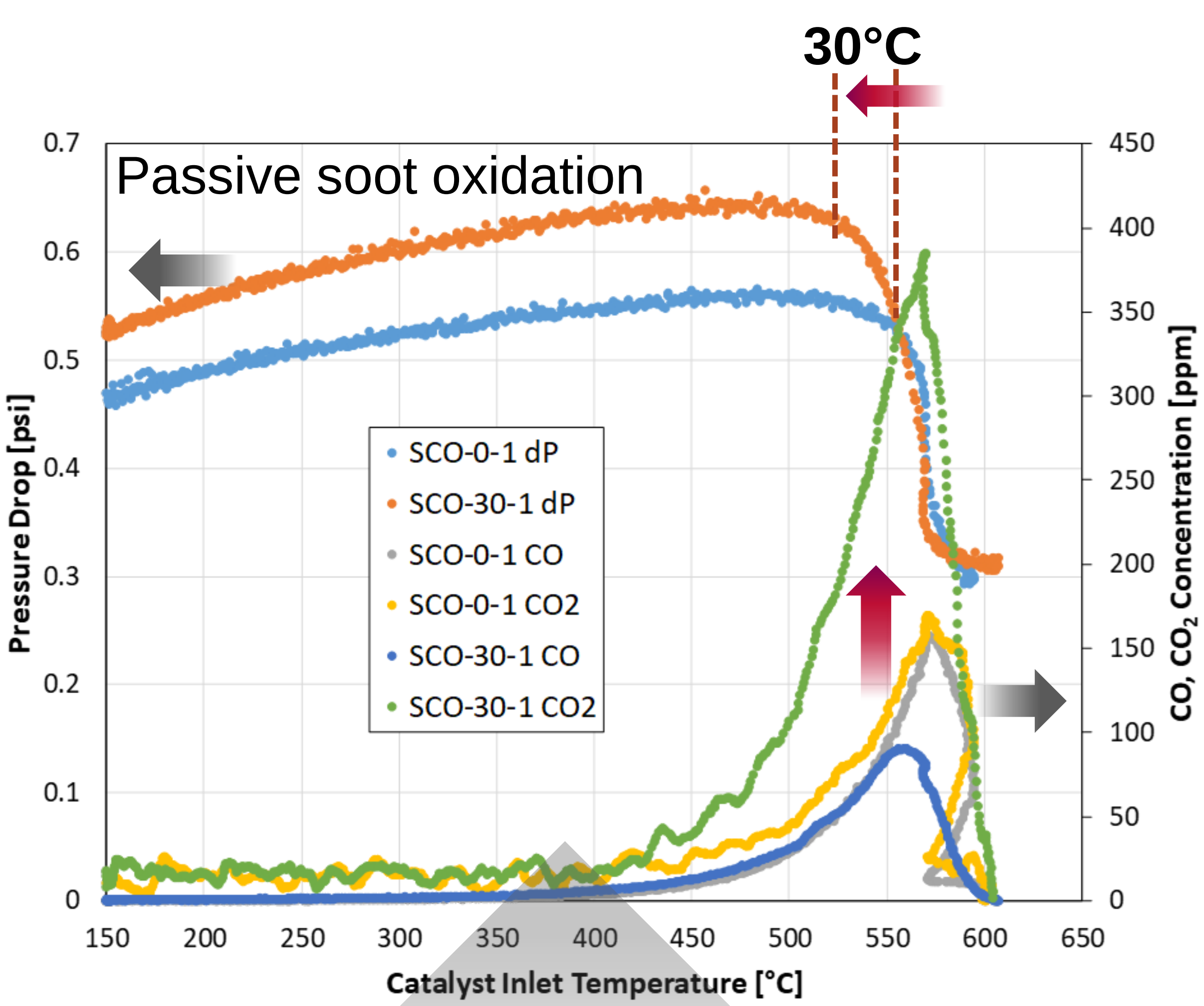
SCO phase positively impacts passive soot oxidation activity and CO/CO_2 production profile

2.76 kg/min 35K GHSV

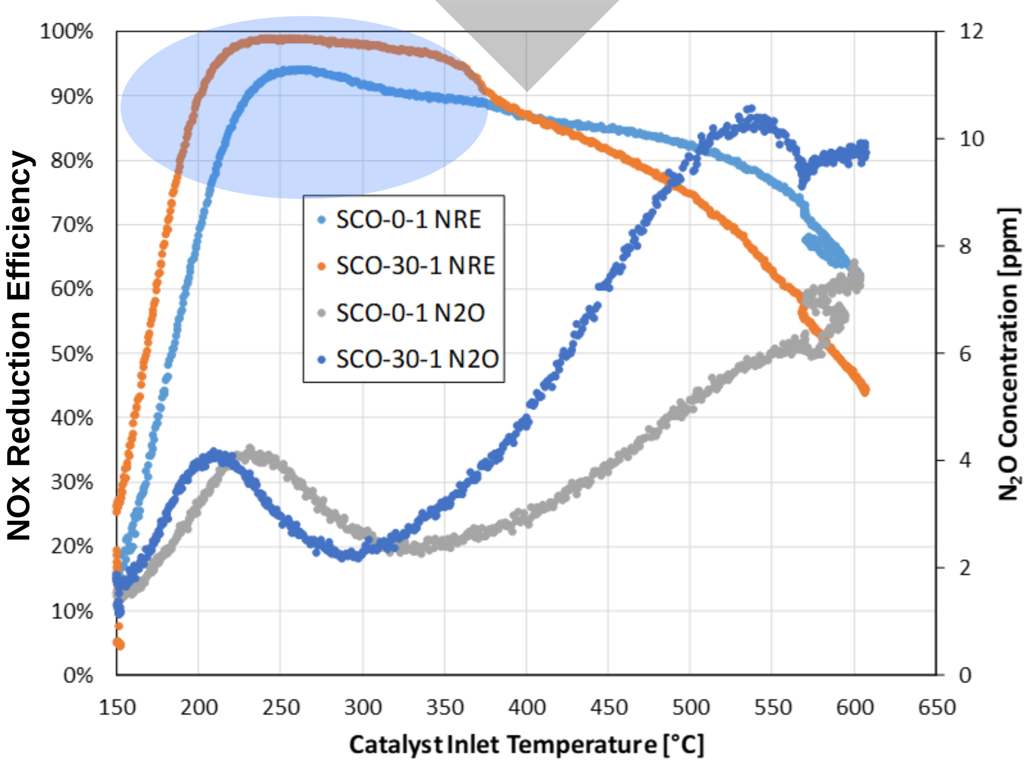
300 ppm NOx & NH_3
10% O_2, 6% H_2O



Std-SCR Conditions



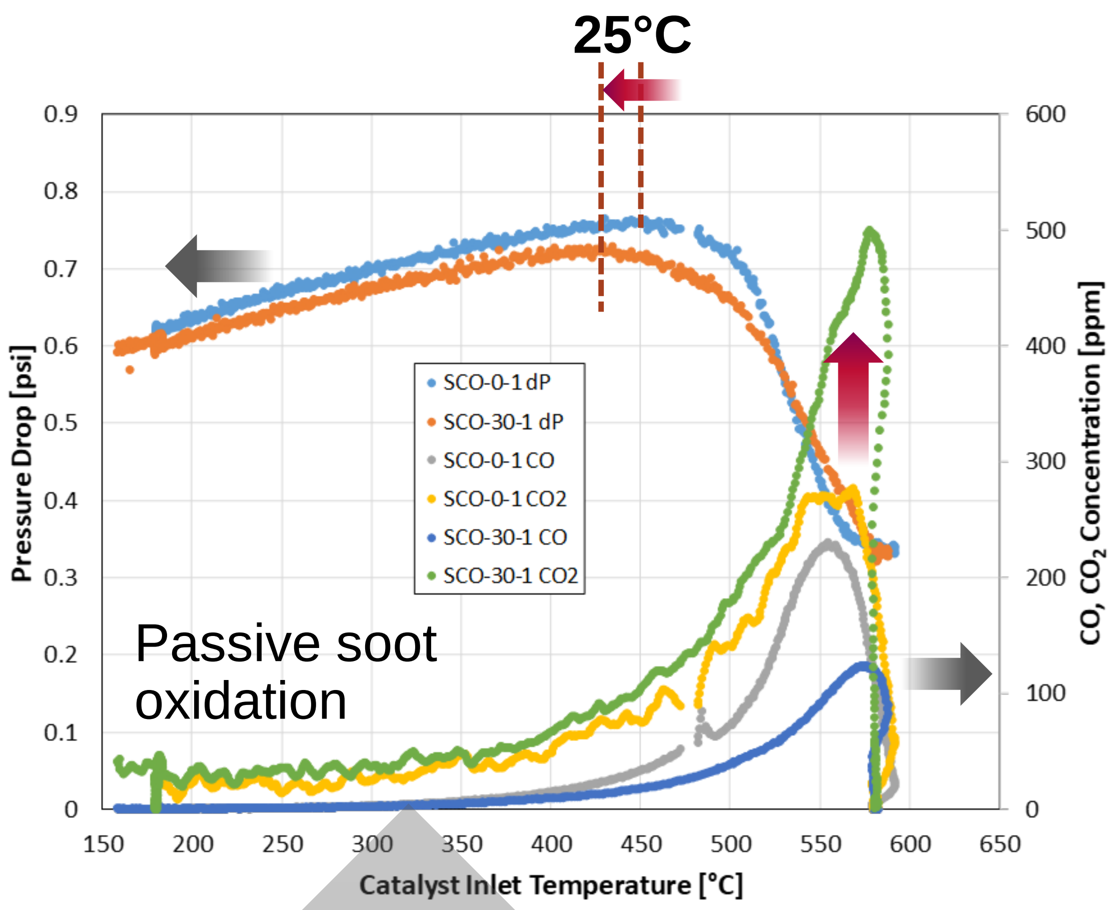
- SCO benefits std-SCR through >350°C



- SCO shifts pressure drop profile to ~30°C lower
- Effluent shifted to CO_2 majority (versus CO production) **

**Important because filter will not have PGM-based CO oxidation

With greater NO_2 in feed, soot oxidation CO/CO_2 product profile becomes main benefit of SCO phase

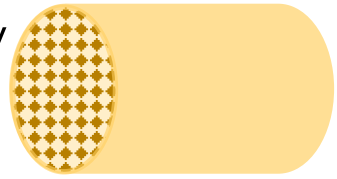


- NO_2/NO_x = 0.35
- ΔP profile to ~30°C lower temperature
- Effluent *heavily* shifted to CO_2 majority**

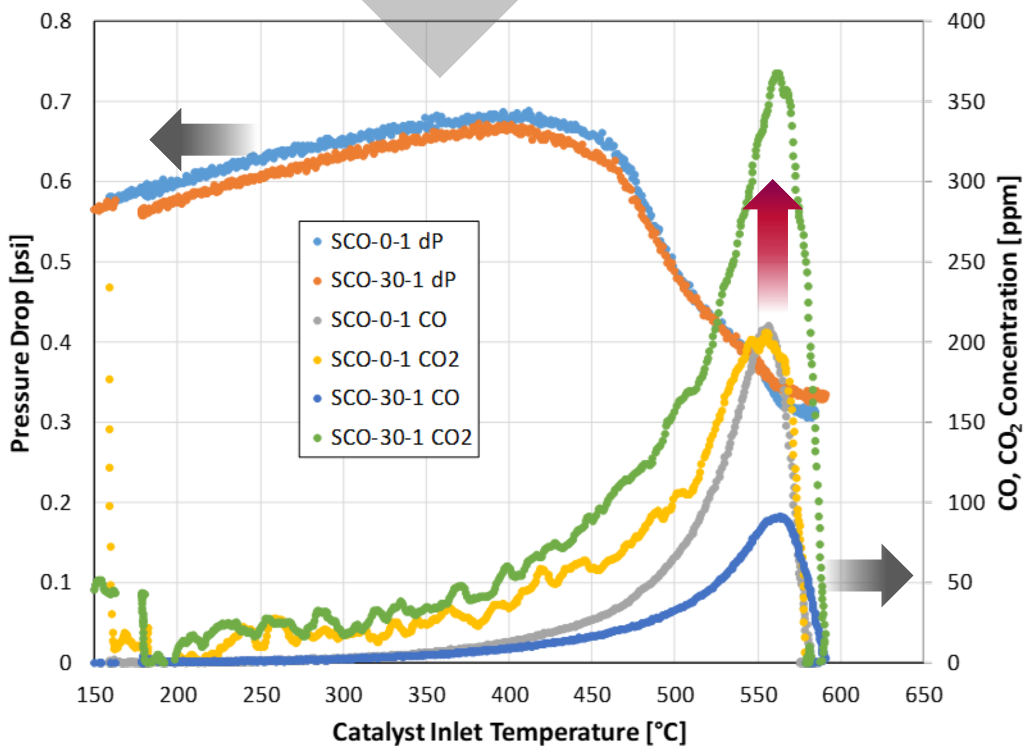
**Important because filter will not have PGM-based CO oxidation

2.76 kg/min 35K GHSV

300 ppm NOx & NH_3
10% O_2, 6% H_2O

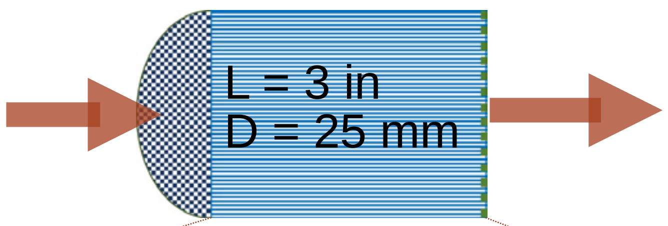


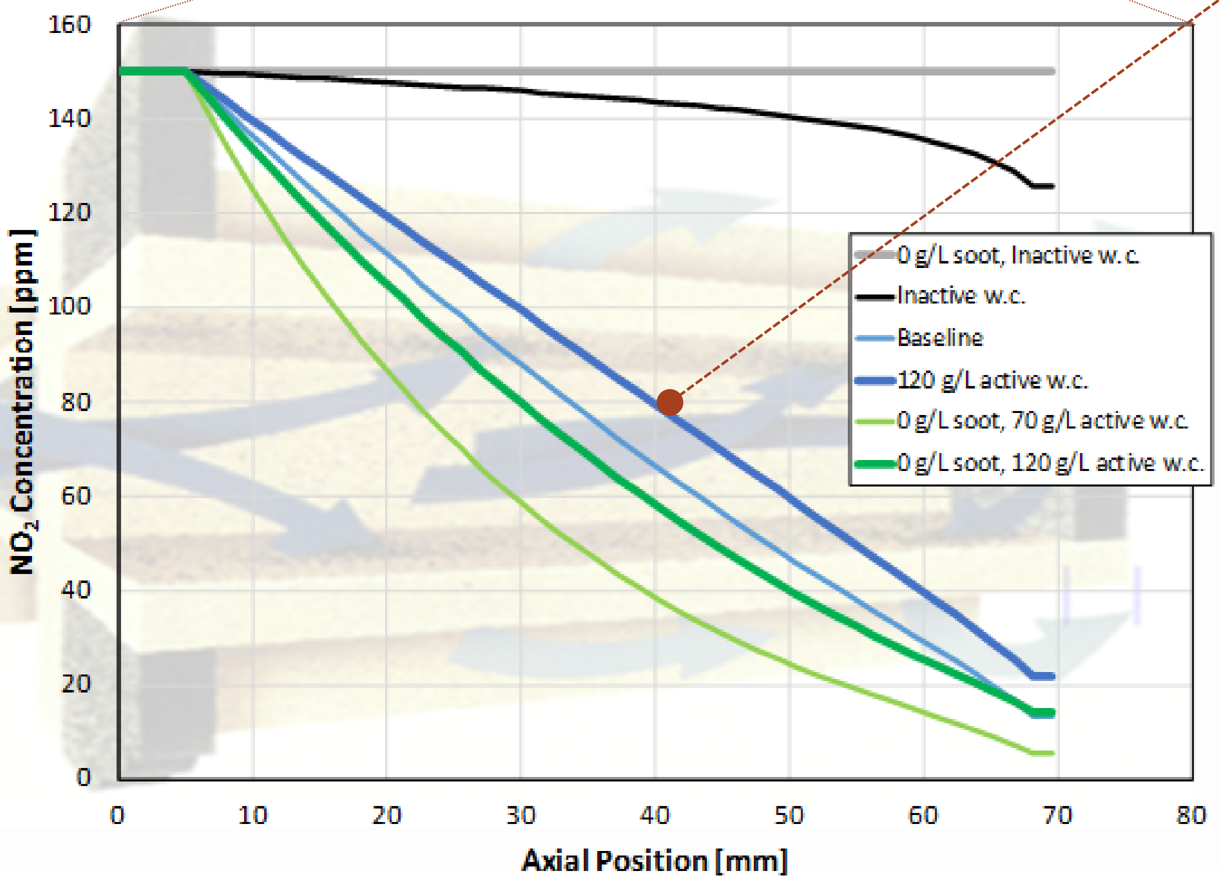
- NO_2/NO_x = 0. 5
- Effluent *__heavily__* shifted to CO_2 majority**



Accomplishments

Axisuite modeling shows the pronounced impact that wall velocity has on diffusive impacts





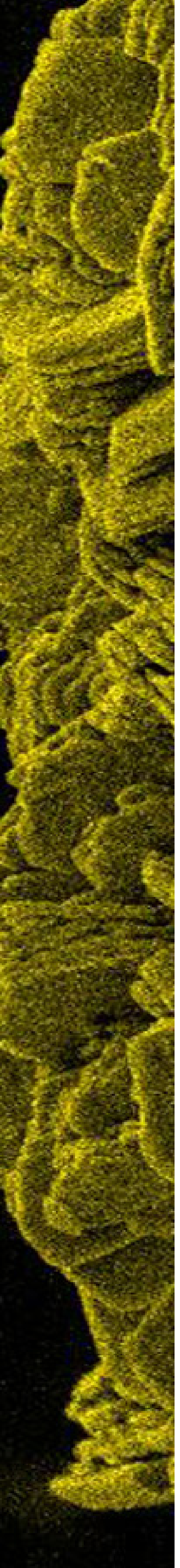
Great SCR catalyst *increases* [NO_2] in inlet channel
- Increases wall flow velocity
- Decreases diffusion contribution

- 250°C
- Baseline: 35K GHSV, 4 g/L soot, 70 g/L active w/c distribution = 1

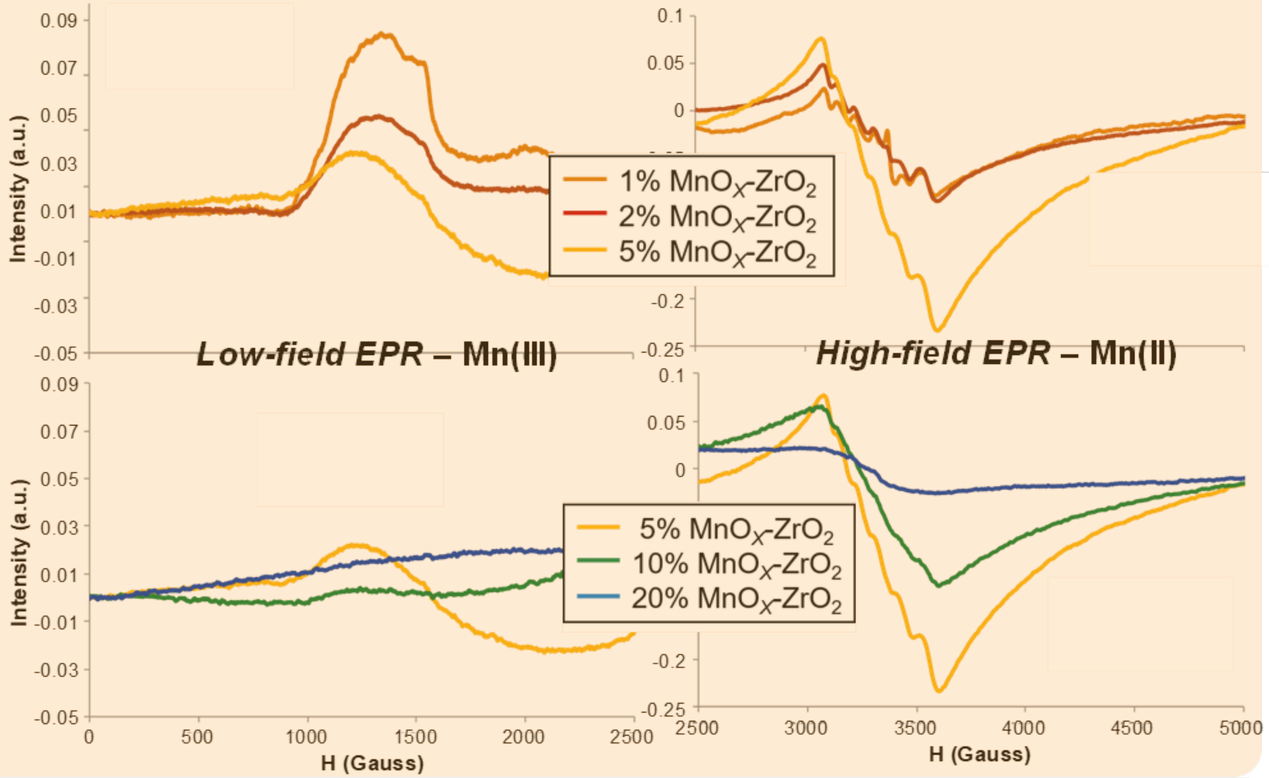
Simulating bench-scale testing of catalyst cores

Accomplishments

Mn-dimer active center, directs pathways for improved thermal and chemical durability

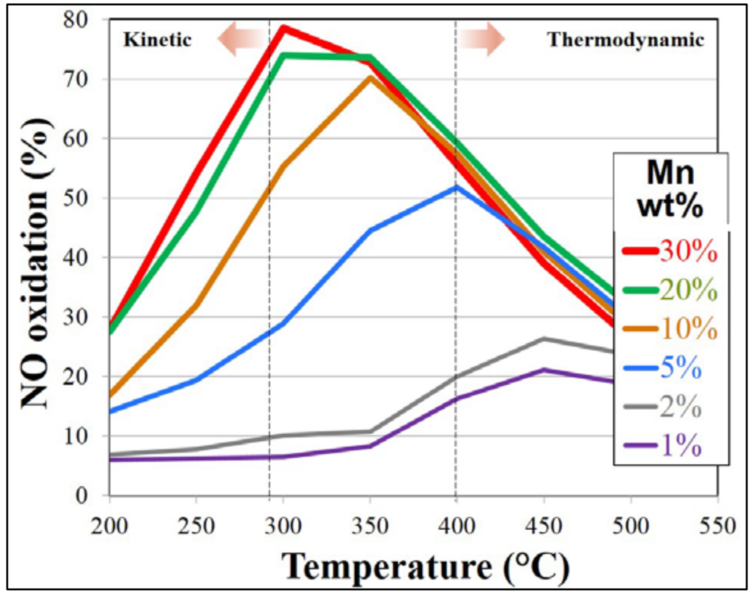


<5% Mn: ↑ Mn = ↑ Mn(II) & ↓ Mn(III) proportionally

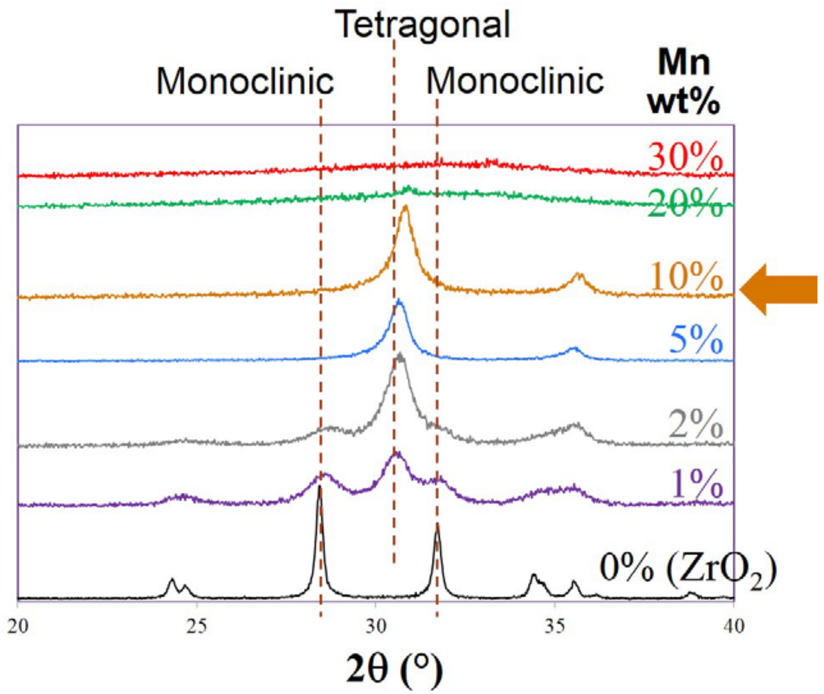


>5% Mn: ↑ Mn = ↓ Mn(II) & ↓ Mn(III) proportionally

- Shift to non-isolated Mn species at 5 wt%
- Optimum NO oxidation at 10 wt% Mn,
- Suggests Mn-dimer active center



10 wt% MnO_2 optimum loading on ZrO_2 for catalyst development

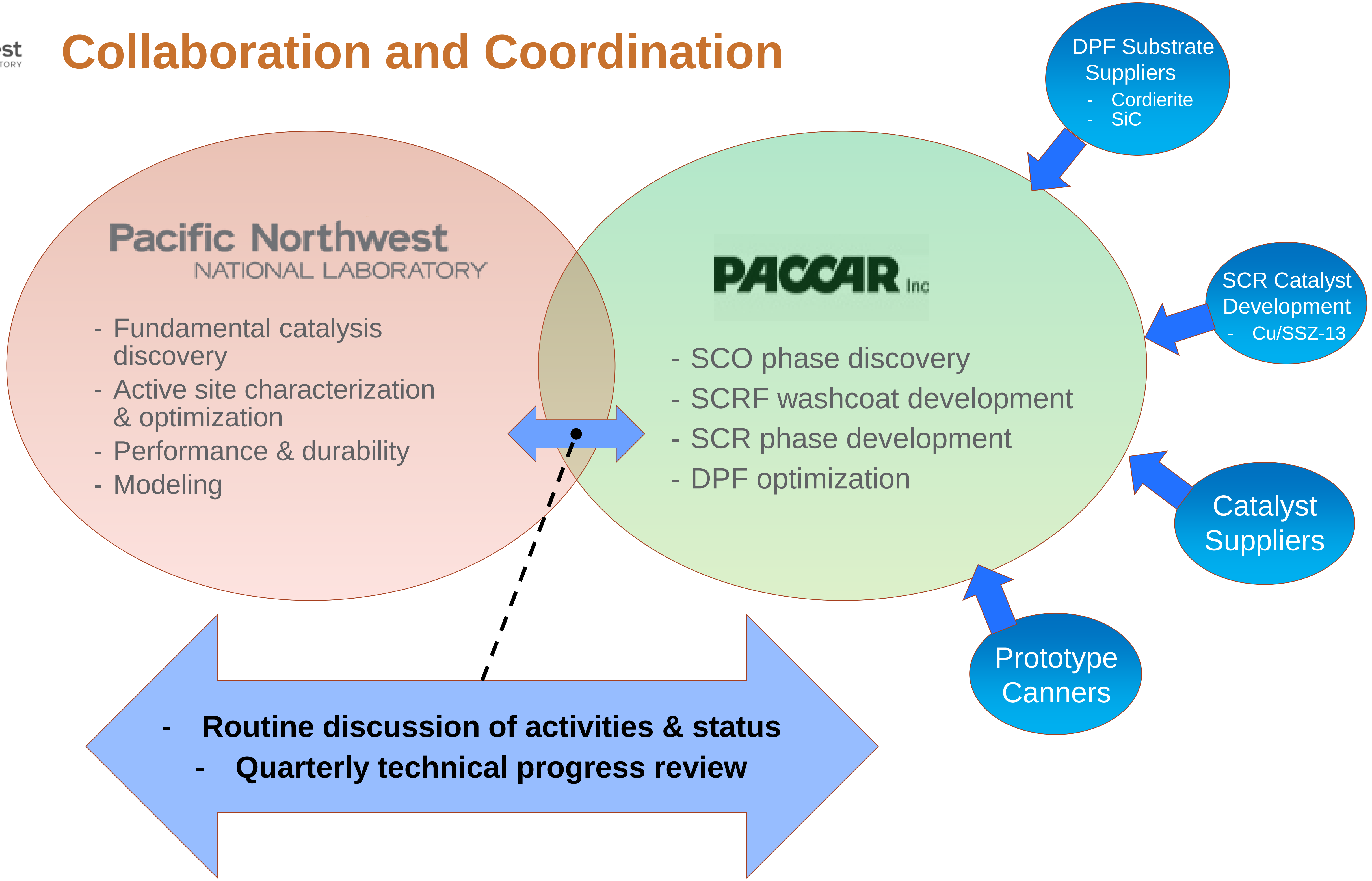


<u>Conditions:</u> 320 ppm NO, 14% O_2, 2.5% H_2O, Balance of N_2, SV=300 L/g-hr

Responses to Reviewer Comments

Comment	Response
Thermal/chemical aging needs to be addressed; GHG emissions (N_2O, CH_4) should be addressed as well	*Reviewer is correct!* Thermal aging has been an area of focus for the work. Last year, showed unique thermally-induced IE aging mechanism (Mn displacing Cu) and relevance to heavy-duty diesel application. N_2O emission profile shown this year. This year sulfur is an area of focus; work is proceeding.
Unclear if "newer" NO_2 formed *in-situ* is not consumed by NH_3.	We can measure it. We are able to track the fate of NH_3 to routes *other* than SCR, e.g., oxidation by CuO clusters. We call this 'parasitic' NH_3 oxidation.
Modest outcome compared to current state-of-the-art which is in industry for >10 years	Yes, SCR-on-DPF is available technology for *light-duty*, enabled by durable CuCHA and high-porosity filter substrates. Not the case for *heavy-duty* . Current technology prohibitively impacts passive soot oxidation and increases aftertreatment fuel penalty.

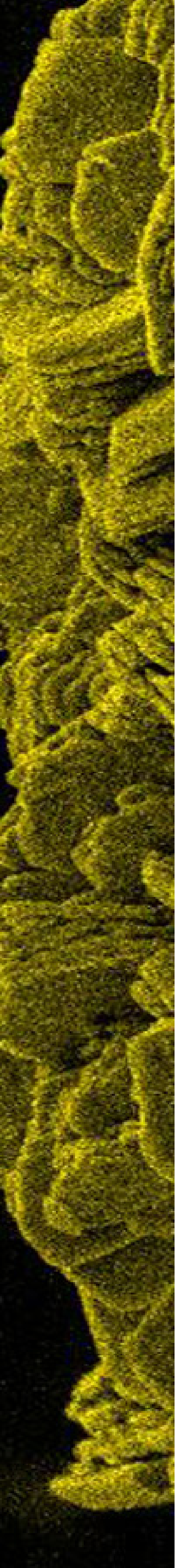
Collaboration and Coordination



Remaining Challenges

- Modeling – Accurately capturing all kinetic pathways of SCO-phase contribution.
  - NO oxidation, STD SCR, FAST SCR, NH3 oxidation
  - Synergistic effect: how do we capture this?

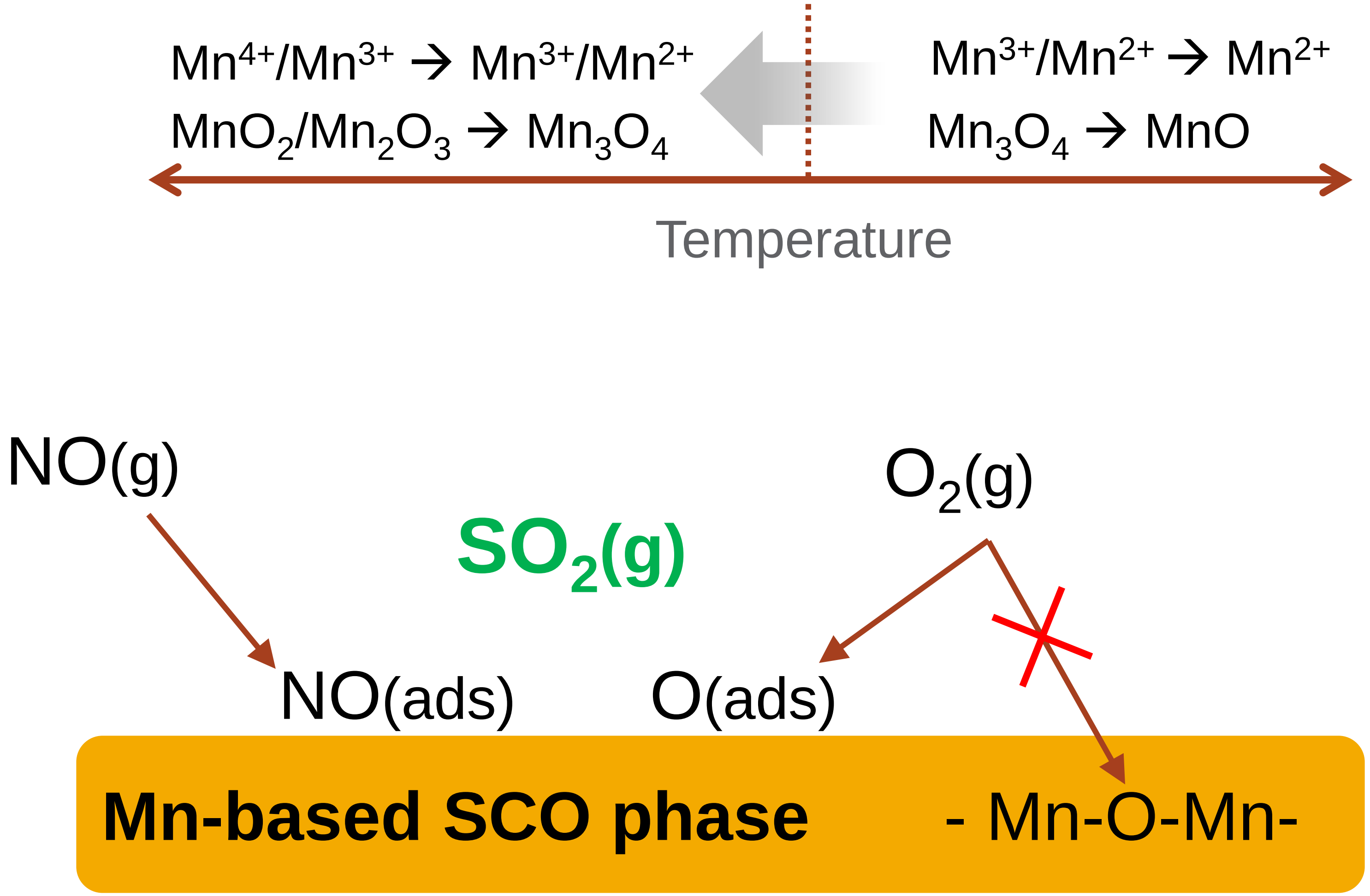
- Chemical poisoning –MnO_X/ZrO_2 solid solution, pursue pathways to address prohibitive interaction if present.



Path Forward

Sulfur durability an area of focus for balance of program

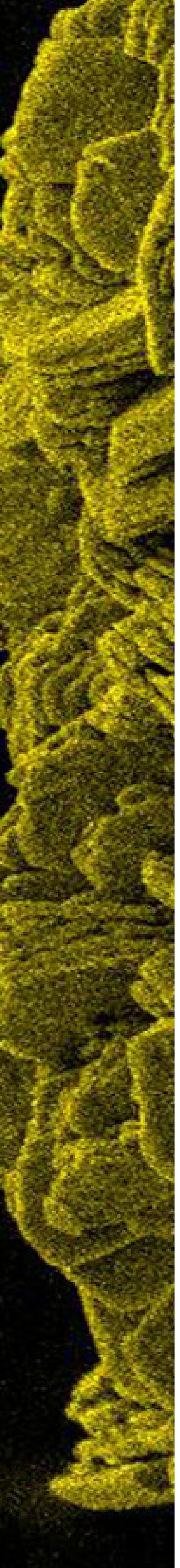
Evidence suggests low-temperature reducibility of Mn may be key to sulfur resistant SCO phase through L-H reaction pathway



$$NO + \tfrac{1}{2} O_2 \xrightarrow[\text{E-R mechanism}]{\text{L-H mechanism}} NO_2$$

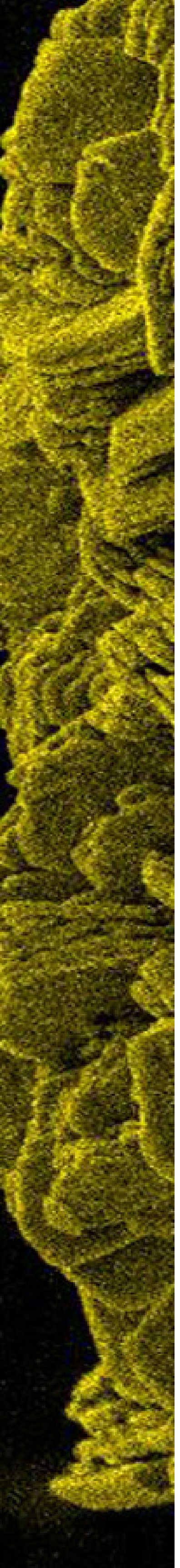
Proposed Future Research

- Model development with full SCO kinetics
- Road-mapping studies with model
- Sulfur durability – SCO-phase modifications for improved reducibility
- Desulfation requirements as *f*(reducibility)



Summary

- 10%Mn/ZrO_2 SCO phase shown to significantly shift NO_2/NO_x balance in the device with equivalent or superior SCR performance.
  - Durable impact on NO_2/NO_x balance across all expected gas compositions
- SCO-SCR synergistic interaction observed from superior low-temperature SCR performance not accounted for by [NO oxidation + SCO-phase SCR]
- SCO phase positively impacts passive soot oxidation activity and CO/CO_2 production profile
  - With greater NO2 in feed, CO/CO_2 product profile becomes main benefit of SCO phase
- Axisuite modeling shows the pronounced impact that wall velocity has on diffusive impacts.
- Mn-dimer active center identified, directs pathways for improved thermal and chemical durability



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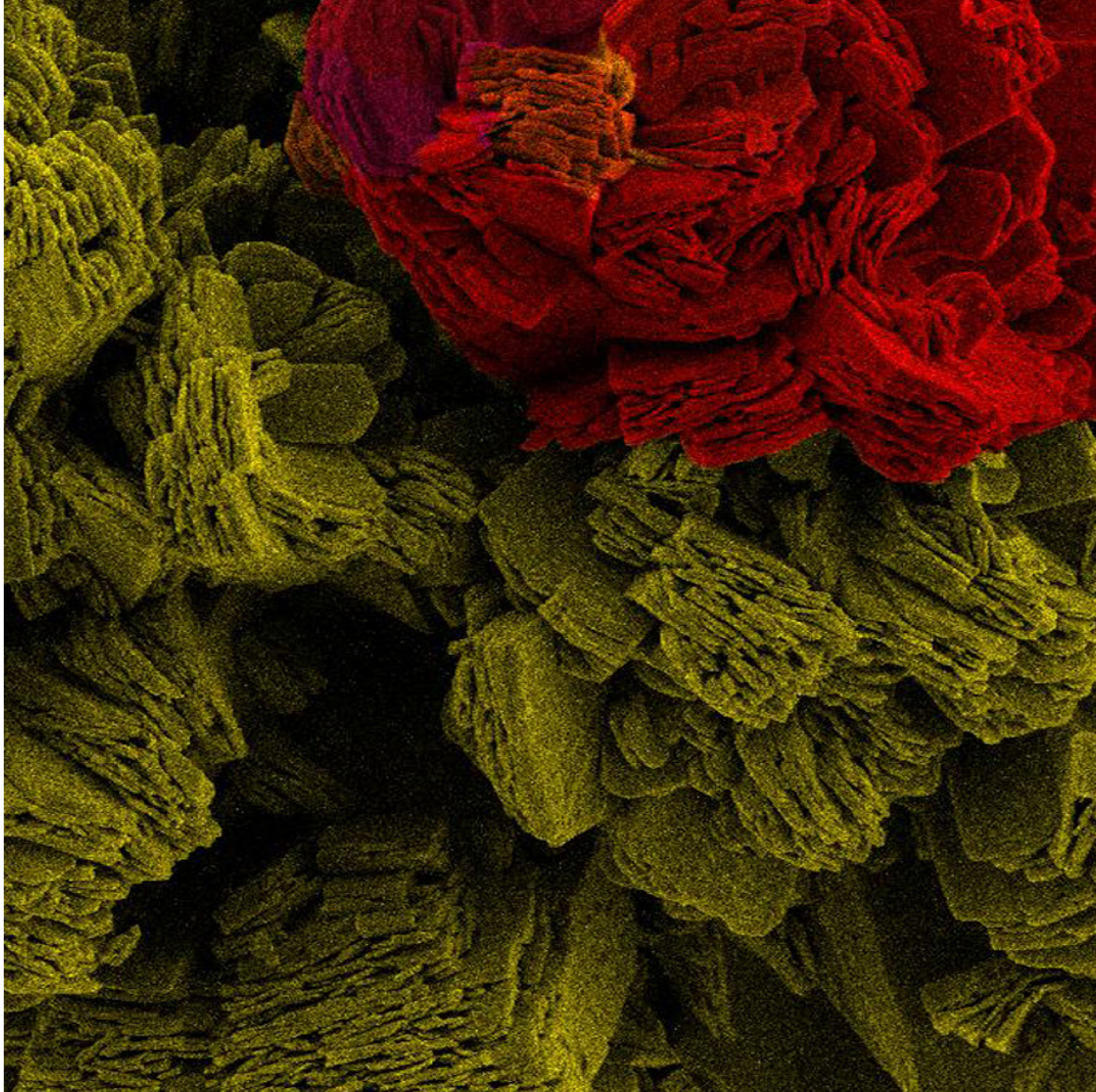
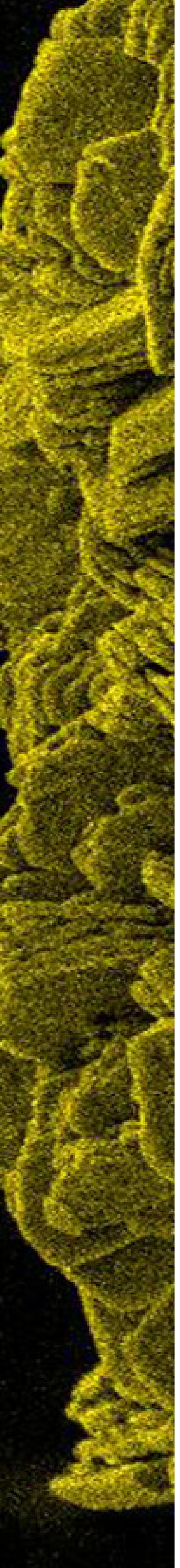
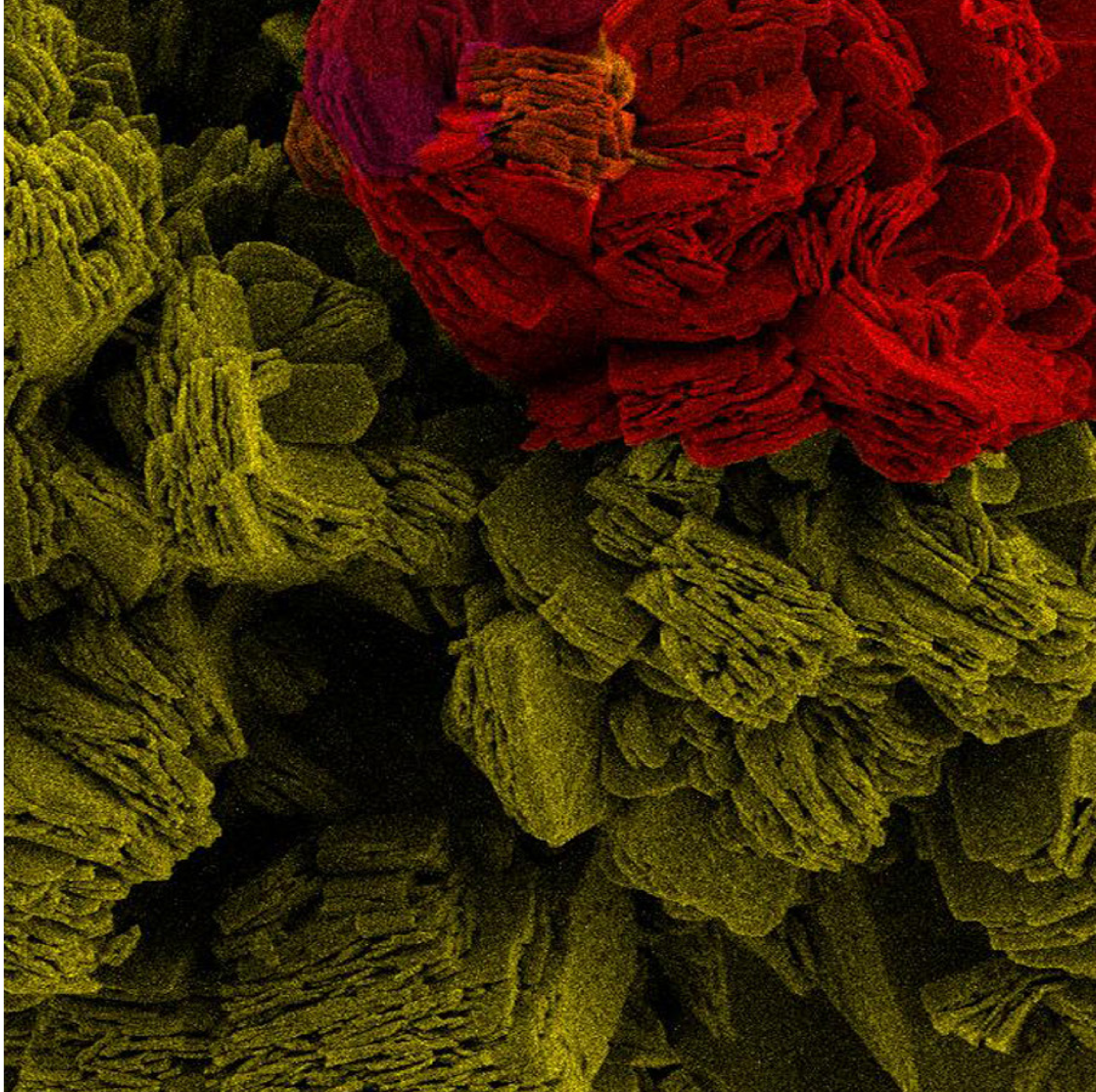
Thank you





Back-up Slides

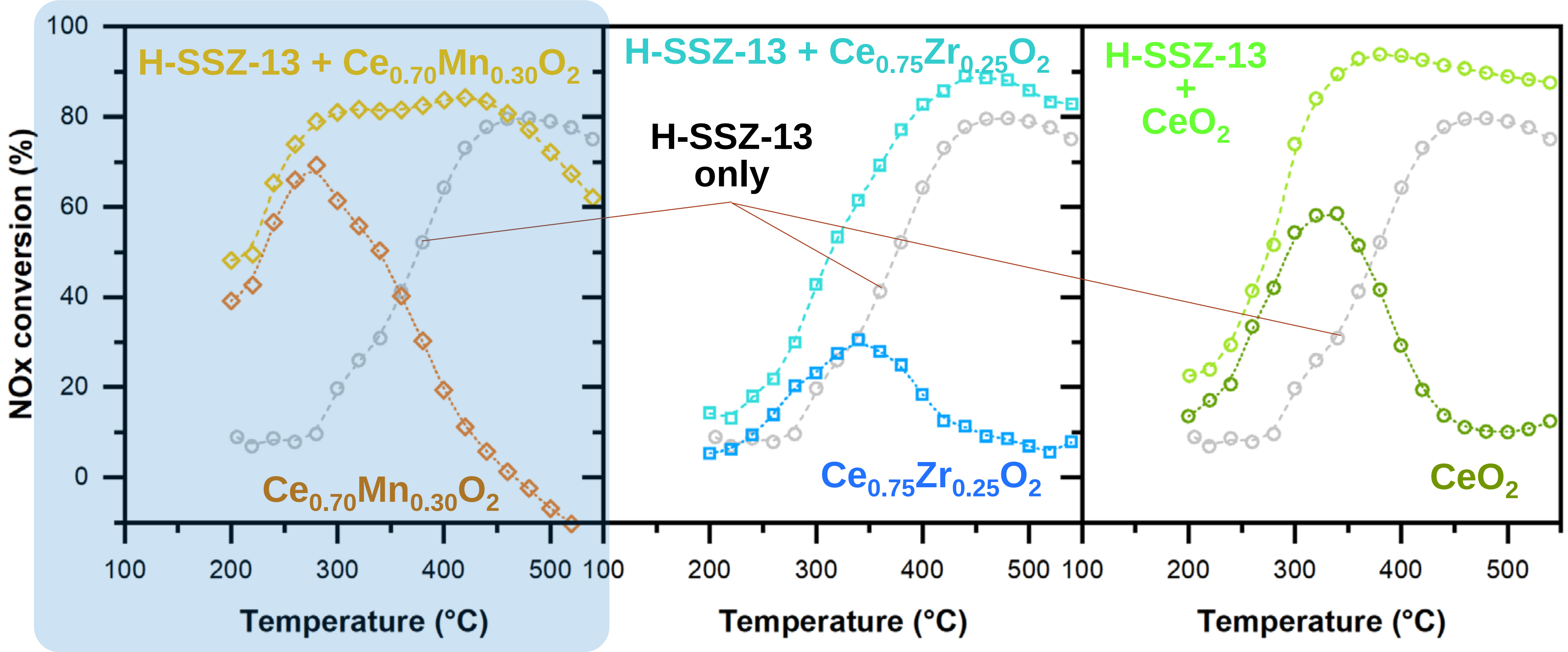


Mn-based SCO showing greatest opportunity for synergistic low-temperature SCR impact

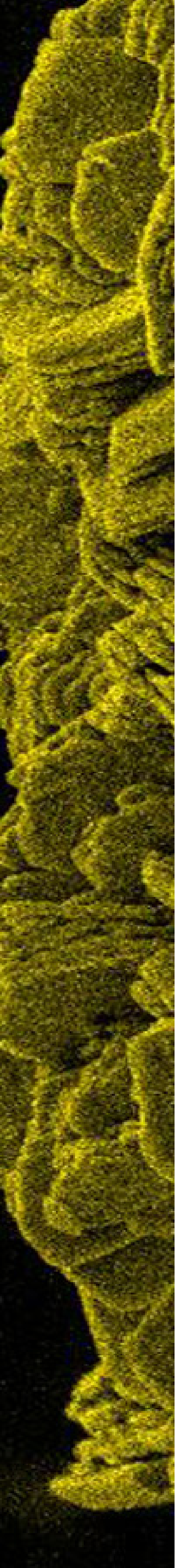
Fast SCR

Fast SCR: 175 ppm NO, 175 ppm NO_2, 350 ppm NH_3, 15% O_2, 6% H_2O and 8% CO_2 (balanced N_2), heating ramp of 2 °C min^{-1}

150 mg catalyst, SV = 400 L g^{-1} h^{-1} (1000 sccm)



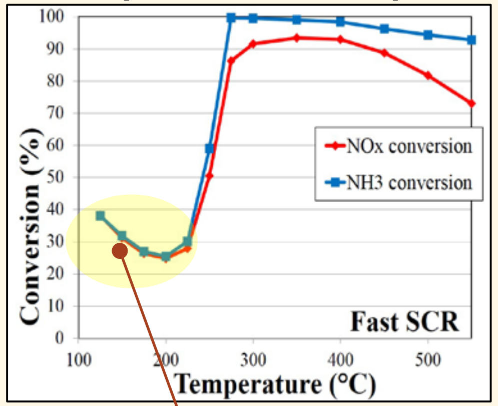
- 10% metal oxide phases co-impregnated onto H-form SSZ-13.
- H-form SSZ-13 (i.e., without Cu) used to highlight NO_2–driven reaction pathways facilitated by the SCO phase.
- Data highlights NO_2 SCR reaction pathways facilitated by SCO phase.



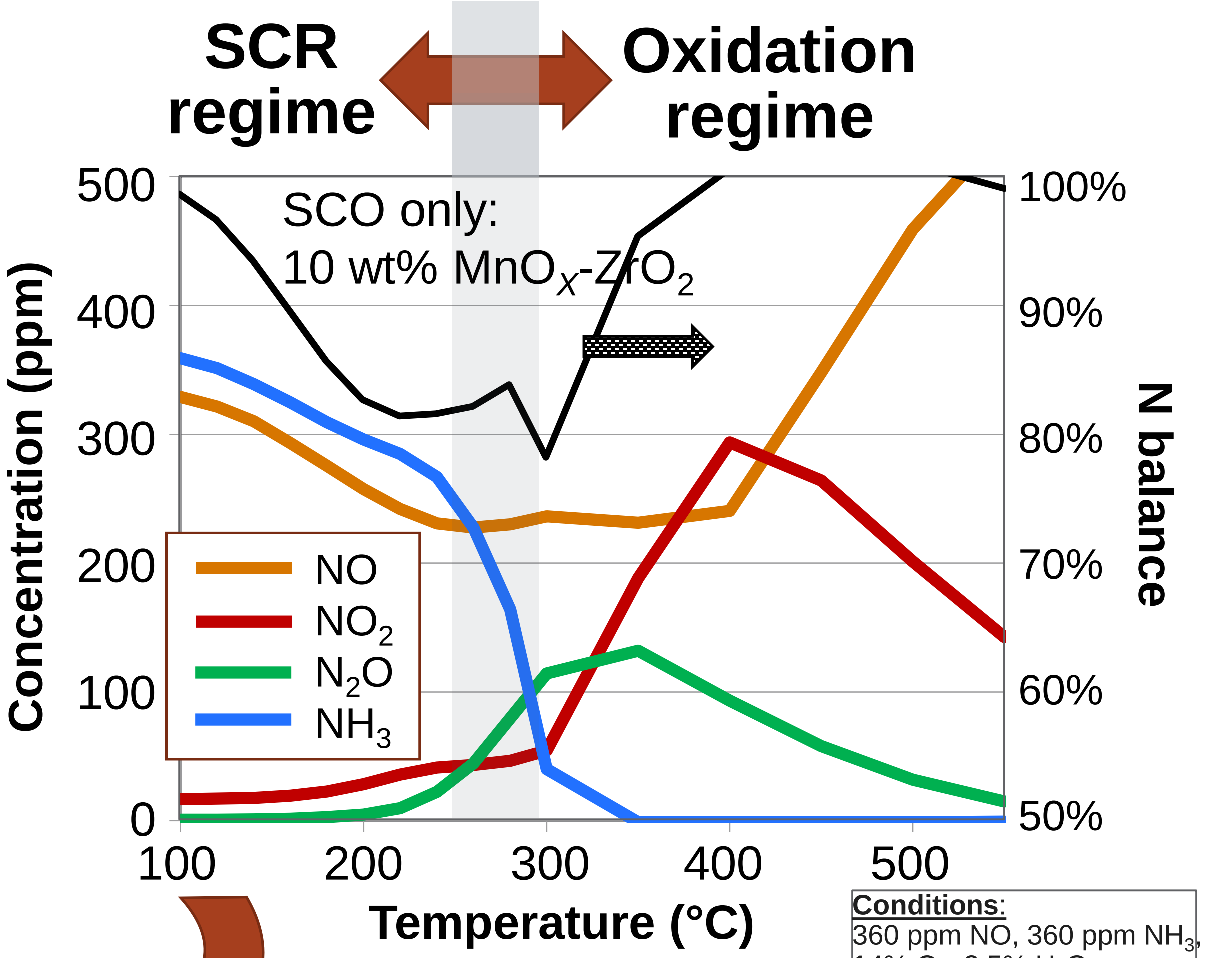
Accomplishments

SCO phase shown to have bi-functionality demonstrating both SCR and oxidation regimes

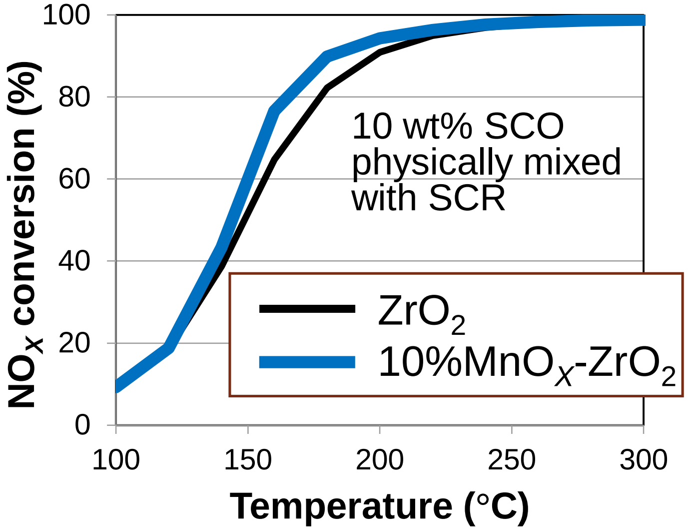
H-SSZ-13
(i.e., no Cu)



Not promoted
Nitrate formation

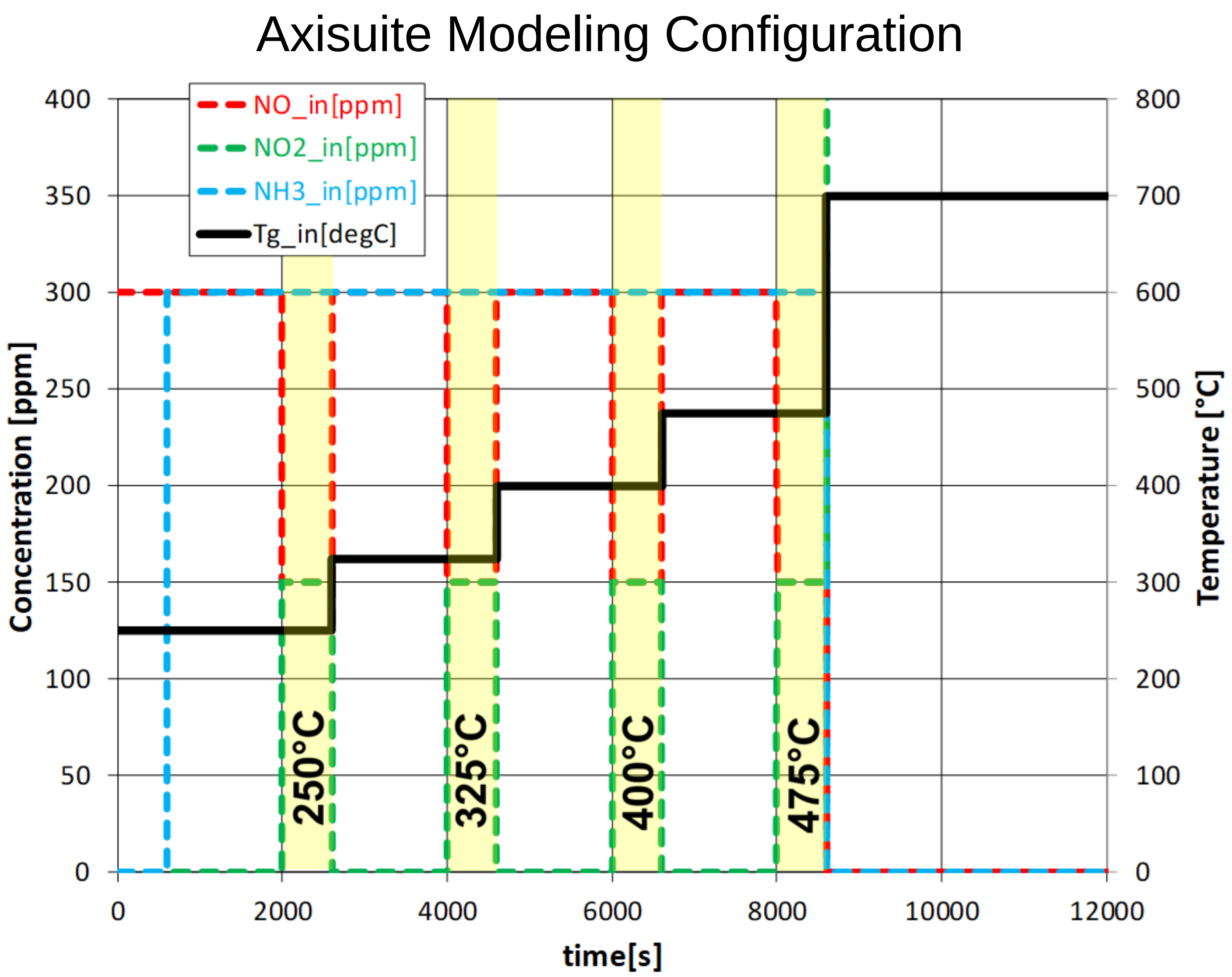


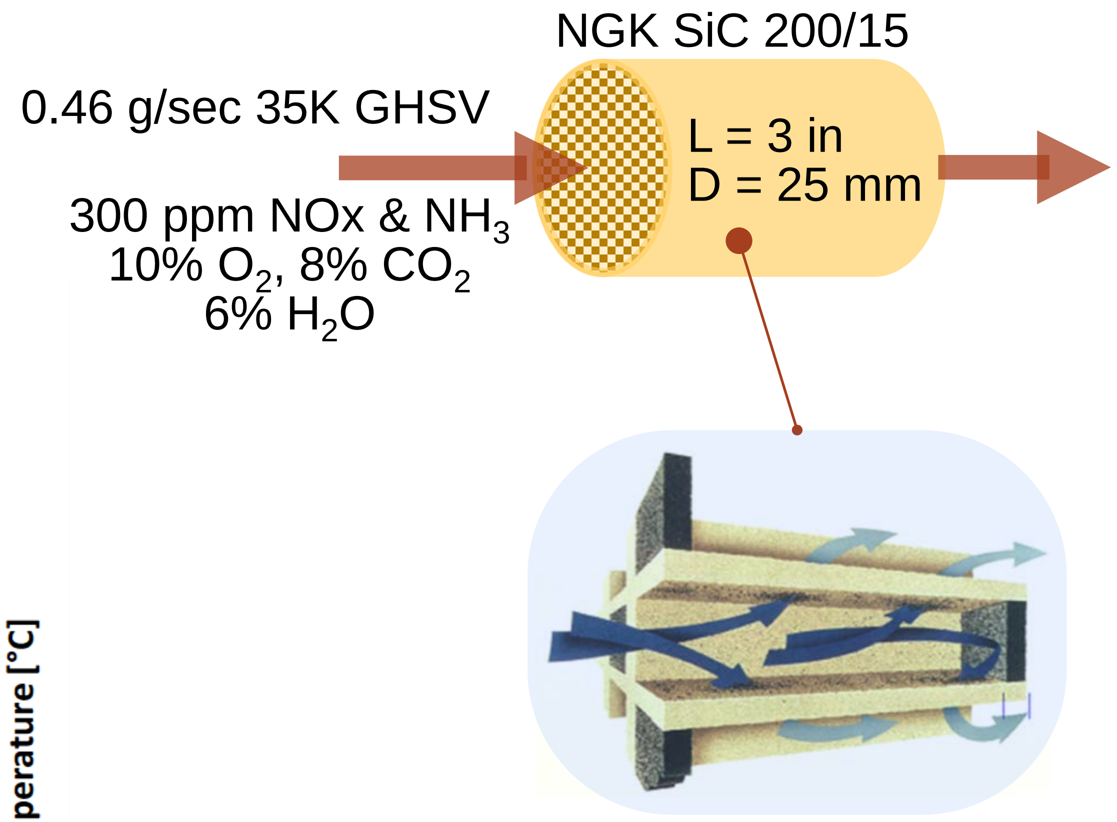
Conditions:
360 ppm NO, 360 ppm NH_3,
14% O_2, 2.5% H_2O,
Balance N_2, SV=300 L/g-hr



SCO phase exhibits low-temperature SCR while promoting higher temperature oxidation function

Axisuite modeling structure built to match bench reactor data





- 4 g/L initial soot loading
- 70 g/L impregnated washcoat loading
- Cu-zeolite Eley-Rideal kinetic scheme

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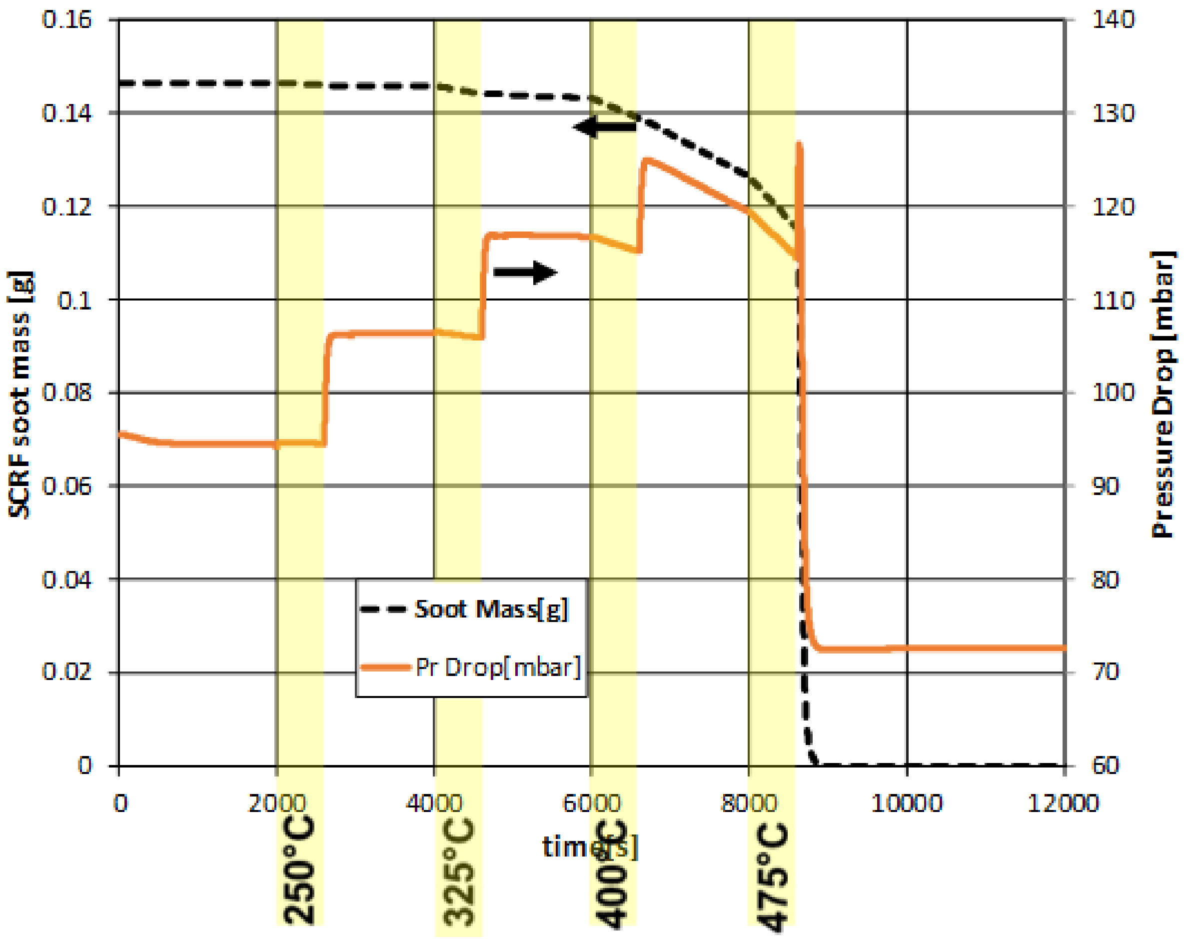
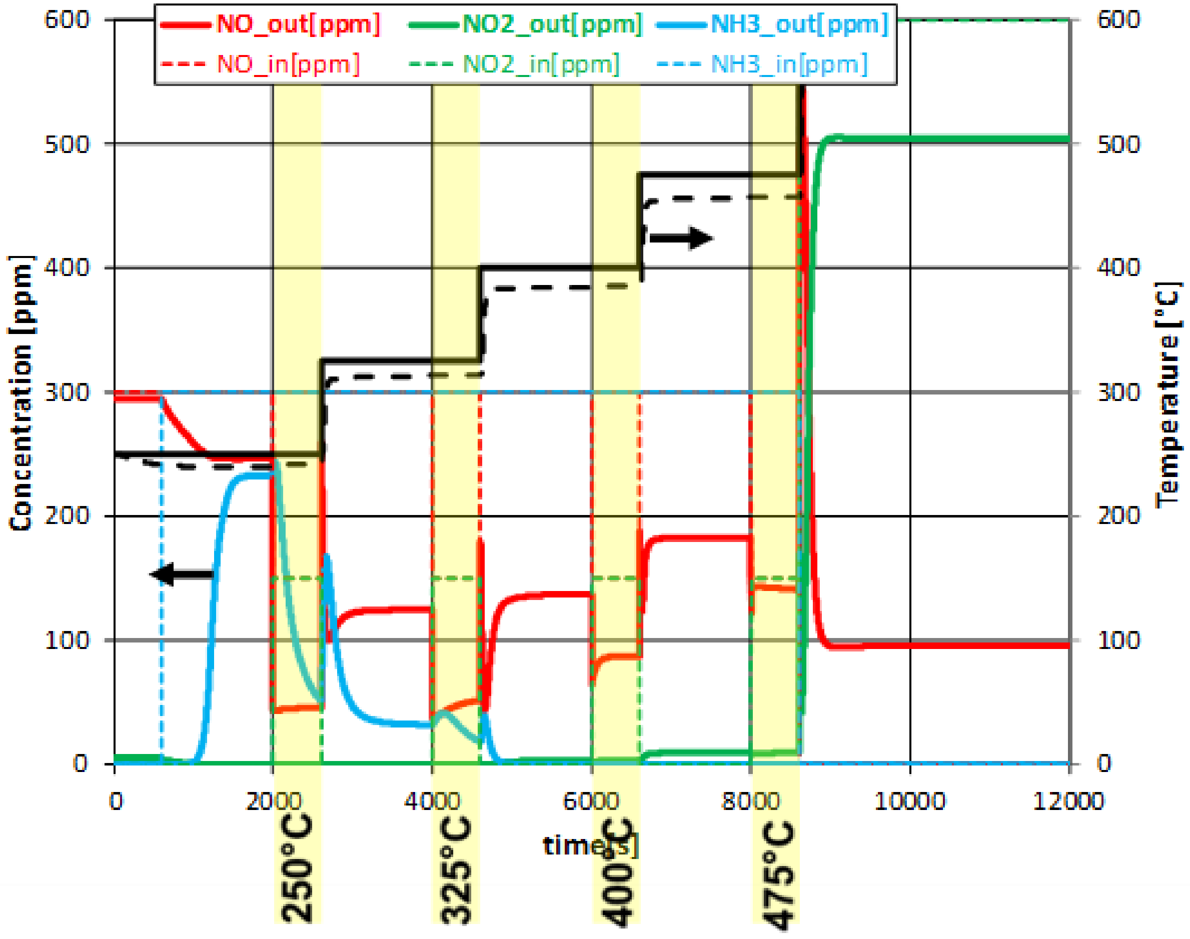
Axisuite modeling has utility for relating soot oxidation activity and SCR performance





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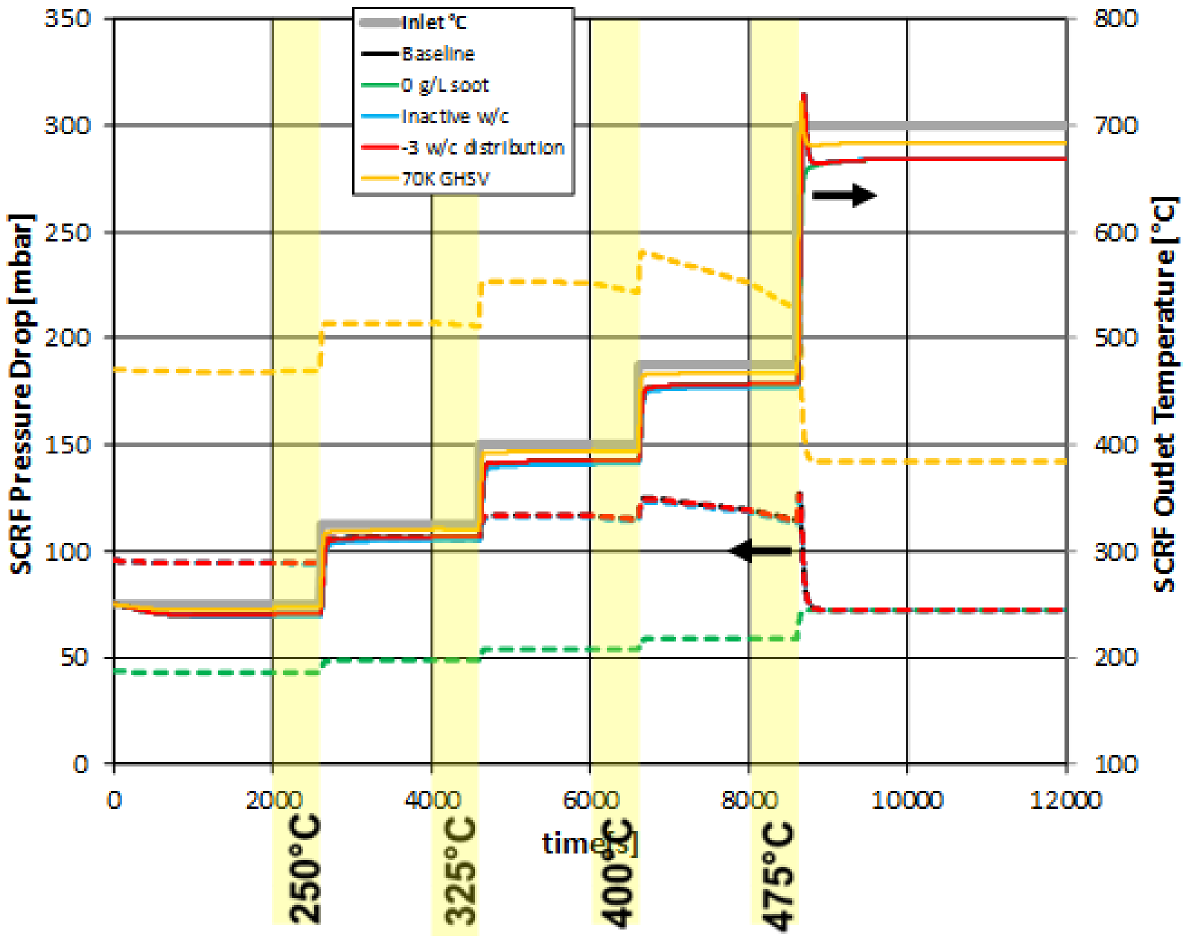
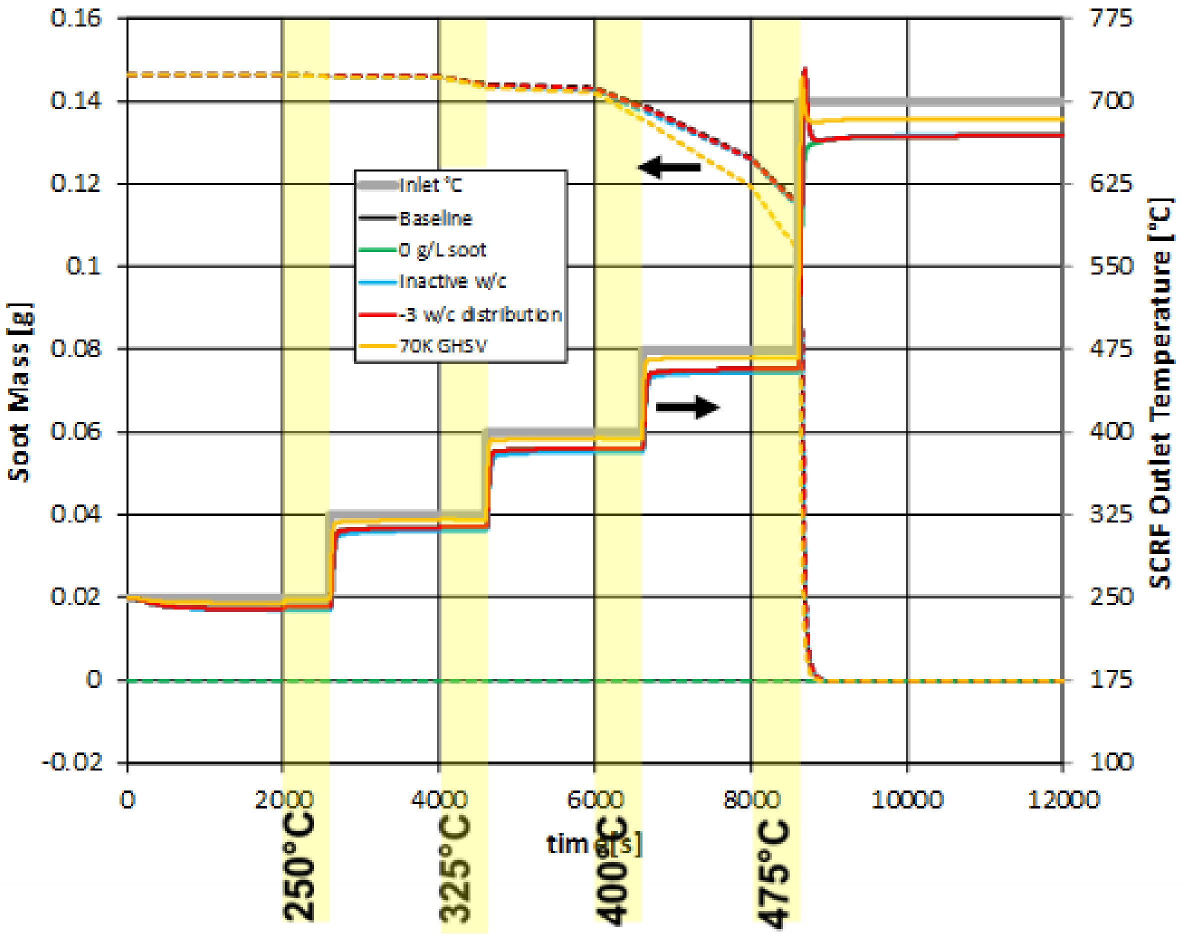
Accomplishments – backup slides

Axisuite modeling has utility for tracking soot oxidation via soot mass and pressure drop





- <insert comment>